

# Influence of Carbon–Chlorine Surface Complexes on the Properties of Tungsten Oxide Supported on Activated Carbons. 1. Dispersion, Distribution, and Chemical Nature of the Metal Oxide Phase

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Different tungsten oxide catalysts supported on chlorinated activated carbons were prepared by using ammonium tungstate and tungsten pentaethoxide as precursor compounds. The supported catalysts were pretreated in wet air at 623 K for 6 h and characterized by N<sub>2</sub> adsorption at 77 K, temperature-programmed desorption, X-ray diffraction, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy. The results indicate that tungsten oxide is anchored to chlorine surface complexes through the formation of W–Cl bonds during either the preparation or wet air pretreatment of the catalysts. This has a major influence on the particle size and distribution of the metal oxide phase supported on the carbon particles.

## Introduction

The surface chemistry of solids used as supports in heterogeneous catalysis can have a great influence on the dispersion, distribution, chemical nature, acid–base character, activity, and selectivity of the catalytic active phase deposited on them. Carbon materials are commonly used as supports for metal catalysts, especially precious metal catalysts, which are widely used to obtain high-value-added chemical products.<sup>1</sup>

A key characteristic of carbon materials is the versatility of their surface chemistry, which can be easily changed by appropriate chemical or thermal treatments to introduce or remove different functionalities or surface complexes. Thus, different oxygen surface complexes can be fixed on carbons by treatment with various oxidizing agents. These oxygen functionalities are bound to the edges of the graphene layers of graphitic microcrystals, and some of them can withdraw electrons from the graphene layers and thereby decrease the Fermi level of the solid,<sup>2</sup> which can affect electronic metal–support interactions.

Furthermore, these oxygen surface complexes increase the surface acidity and hydrophilicity of carbons and can be gradually removed by heat treatment in an inert atmosphere, decreasing the surface acidity and the hydrophilicity.<sup>3</sup> Oxygen surface complexes of acid character, such as carboxyl and phenolic groups, are especially important in the adsorption of metal ions from aqueous solutions.<sup>4</sup> In this case, the metal ions are anchored to the oxygen surface complexes, so that a homogeneous distribution of the metal ions on the carbon surface can be achieved under the appropriate experimental conditions.

The influence of carbon oxygen surface complexes on the dispersion and catalytic activity of metals has been widely studied by different authors and is the object of numerous

published studies.<sup>1</sup> In contrast, the influence of other heteroatoms has been far less studied.

Nitrogen surface complexes can be introduced by treatment with ammonia at moderate temperatures.<sup>5</sup> Some nitrogen functionalities so introduced increase the electronic density of the graphene layers because they behave as Lewis bases. Thus, it has been shown<sup>6,7</sup> that the introduction of these groups in activated carbons leads to an increase in their sulfur dioxide oxidation activity. Studies have also been published on the effect of these groups on the characteristics of iron,<sup>8</sup> ruthenium,<sup>8</sup> and molybdenum supported<sup>9,10</sup> on activated carbons.

Finally, chlorine surface complexes are introduced on carbons by heat treatment with chlorine gas at moderate temperatures.<sup>5</sup> These groups increase the surface acidity of carbons<sup>11–13</sup> and their hydrophilicity, and they are thermally more stable than the oxygen surface complexes of acidic character.<sup>13</sup> Chlorinated activated carbons were recently used<sup>13</sup> as catalysts for the decomposition reaction of 2-propanol, and the dehydration activity was observed to decrease with an increase in chlorine content. To our best knowledge, chlorinated activated carbons have not been used as support for catalysts. With this background, we designed a study to determine the effect of the chlorine surface complexes of activated carbons on the properties of tungsten oxide catalysts deposited on them. This work forms part of a wider study we are conducting on the tungsten/carbon system.<sup>14–18</sup>

## Experimental Section

An activated carbon was prepared from olive stones by carbonization of the raw material at 1123 K for 15 min in N<sub>2</sub> flow (300 cm<sup>3</sup>/min), and activation at 1123 K for 4 h in CO<sub>2</sub> flow (300 cm<sup>3</sup>/min) to 22% of burnoff. The activated carbon thus obtained was sieved again and the particle size between 1 and 2 mm was used. This sample, with an ash content of 0.4%, will be referred to hereafter as H.

Activated carbon H was chlorinated at either 473 or 673 K using a chlorine flow obtained from the reaction of potassium

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**TABLE 1: Tungsten Content of the Supported Catalyst**

catalyst	% W
HWe	6.9
H1We	7.5
H2We	7.7
HWa	7.4
H1Wa	7.4
H2Wa	8.1

permanganate with hydrochloric acid (reagent grades). The chlorine flow was purified by bubbling through two traps containing water and sulfuric acid, respectively, and finally it was dried through another trap containing dryerite. Prior to the chlorination, the carbon H was treated at 573 K in nitrogen flow for 30 min. The temperature was then set at either 473 or 673 K and the N<sub>2</sub> flow was switched to Cl<sub>2</sub> flow, which was maintained for 30 min. After this treatment, the Cl<sub>2</sub> flow was switched back to N<sub>2</sub> flow and the chlorinated samples were heated at 673 K for 45 min. The samples were then cooled to room temperature. Samples prepared at 473 and 673 K are referred to hereafter as H1 and H2 samples, respectively. The chlorine content of the samples was determined by following a method described elsewhere<sup>11</sup> and was 8.4% for H1 and 11.0% for H2.

The catalysts were prepared from two different precursors, ammonium tungstate and tungsten pentaethoxide. The preparation of the catalyst from (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> was by impregnation of the support with an aqueous solution of the above salt, as described in detail elsewhere.<sup>15</sup> The preparation of the catalyst from W(OEt)<sub>5</sub> was carried out by adsorption from an *n*-hexane solution of the alkoxide. For this purpose, the activated carbon was outgassed under vacuum at room temperature for 1 h. The appropriate amount of alkoxide was then dissolved in the minimum amount of *n*-hexane required to cover the activated carbon and was injected through a septum in the flask containing the support. After 12 h of contact time, the residue of the solvent was eliminated in N<sub>2</sub> flow at room temperature. Finally, the catalyst was dried overnight at 383 K.

We were unable to prepare catalysts based on tungsten hexacarbonyl because the carbonyl was not adsorbed into the chlorinated support after application of the sublimation technique, described elsewhere.<sup>15</sup>

The prepared catalysts will be referred to hereafter by adding Wa (from ammonium tungstate) or We (from tungsten pentaethoxide) to the name of the support.

The exact tungsten content of the supported catalyst was determined in a thermobalance by burning a portion of the catalyst in a flow of air at 1073 K until constant weight. The residue left was identified, by X-ray diffraction, as tungsten trioxide, from which the tungsten content of the catalysts was obtained and it is compiled in Table 1.

Before the catalysts were characterized, they were heated in wet air at 623 K for 6 h. The wet air was obtained by saturation of an air flow with water at 298 K. Once the treatment was finished, the samples were cooled to the desired temperature in dry air.

Characterization of the supported catalysts was carried out by the following methods: N<sub>2</sub> adsorption at 77 K, from which the BET surface area was obtained; temperature-programmed desorption (TPD); X-ray diffraction (XRD); high-resolution transmission electron microscopy (HRTEM); and X-ray photoelectron spectroscopy (XPS).

TPD was carried out by heating the samples at different temperatures up to a maximum of 1273 K in He flow (60 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate of 50 K min<sup>-1</sup>. The amount of evolved

**TABLE 2: BET Surface Area of the Supports and Supported Catalysts after Pretreatment in Wet Air at 623 K for 6 h**

sample	S <sub>N2</sub> (m <sup>2</sup> g <sup>-1</sup> )
H1	543
H2	581
H1We	587
H2We	603
H1Wa	602
H2Wa	583

**TABLE 3: Mean Particle Size,  $\phi$ , of Tungsten Oxide in Supported Catalysts Pretreated in Wet Air at 623 K for 6 h**

catalyst	$\phi$ (nm)
HWe	54
H1We	54
H2We	36
HWa	111
H1Wa	82
H2Wa	75

gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube), as described elsewhere.<sup>15</sup>

XRD patterns were recorded with a Phillips PW1710 diffractometer using Cu K $\alpha$  radiation. JCPDS files were searched to assign the different diffraction peaks observed.

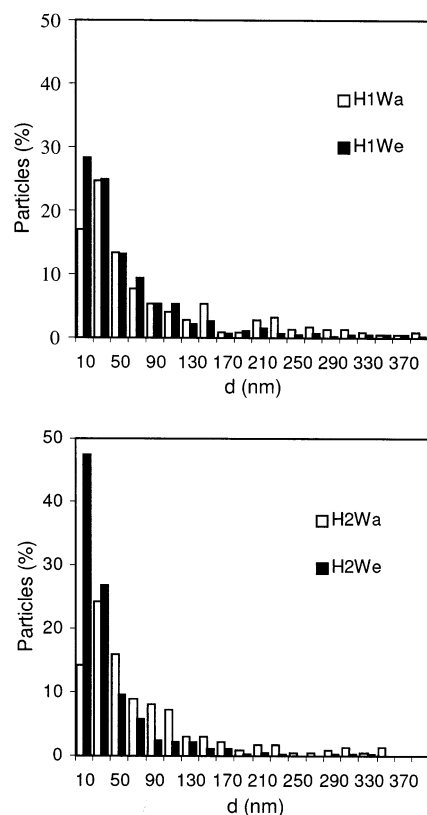
HRTEM was carried out with Phillips CM-20 equipment that used an EDAX microanalysis system. Magnification was 600000 $\times$ , and maximum resolution was 0.27 nm between points and 0.14 nm between lines.

XPS measurements were made with an Escalab 200R system (VG Scientific Co.) with Mg K $\alpha$  source ( $h\nu = 1253.6$  eV) and hemispherical electron analyzer. Prior to the analysis, the samples were pretreated in situ at 623 K for 6 h in He, dry air, or wet air. Once the treatment was finished, the samples were cooled to the desired temperature in the same flow, except in the case of the samples treated in wet air, which was changed to dry air. They were then evacuated at high vacuum and introduced into the analysis chamber. A base pressure of 10<sup>-9</sup> Torr was maintained during data acquisition. Survey and multiregion spectra were recorded at C<sub>1s</sub>, N<sub>1s</sub>, O<sub>1s</sub>, and W<sub>4f</sub> photoelectron peaks. Each spectral region of photoelectron interest was scanned several times to obtain good signal-to-noise ratios. The spectra obtained after background signal correction were fitted to Lorentzian and Gaussian curves to obtain the number of components, the position of the peak, and the peak areas. All binding energies were measured with regard to that of the graphitic C<sub>1s</sub> peak, taken<sup>19</sup> as 284.9 eV.

## Results and Discussion

Table 2 exhibits the BET surface area of the chlorinated supports and supported catalysts after their pretreatment in wet air at 623 K. The S<sub>N2</sub> values of the supported catalysts were similar to or slightly higher than those of their corresponding supports. There was, therefore, no blocking of porosity by the metal oxide phase.

The mean particle size ( $\phi$ ) of the supported catalysts after their wet air pretreatment was calculated from particle size distributions obtained by HRTEM (see, for example, Figure 1). According to these results (Table 3), the catalysts from the We series had a lower  $\phi$  value, i.e., higher dispersion, than those from the Wa series. The term dispersion should be used in this context as a parameter that is inversely related to the metal oxide particle size. In addition, an increase in the chlorine content of



**Figure 1.** Particle size distribution of supported catalysts pretreated in wet air at 623 K for 6 h, obtained by HRTEM.

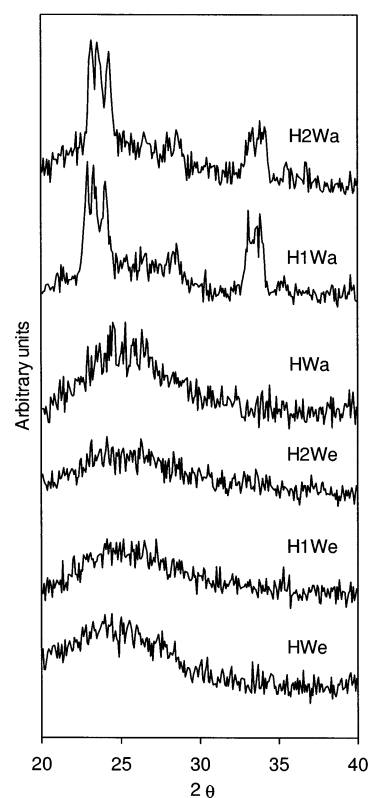
**TABLE 4: Amounts of H<sub>2</sub>, CO, and CO<sub>2</sub> (μmol g<sup>-1</sup>) Desorbed to 1273 K from Supports and Supported Catalysts after Pretreatment in Wet Air at 623 K for 6 h**

sample	H <sub>2</sub>	CO	CO <sub>2</sub>	Q
H	10	2429	298	-
H1	4	2101	323	-
H2	2	2182	338	-
HWe	28	3197	523	1218
H1We	7	3495	527	1804
H2We	1	4394	667	2870
HWa	22	2990	368	700
H1Wa	4	3046	325	950
H2Wa	3	2926	319	706

the support decreased the  $\phi$  value in the We series but had practically no influence on this value in the Wa series.

XRD patterns of the above catalysts are depicted in Figure 2. The We-series catalysts showed no diffraction peak corresponding to the metal oxide phase, indicating that these supported catalysts are formed by very thin sheets or films with very low crystallinity. The same result was found for catalyst HWa. However, well-defined diffraction peaks corresponding to rhombic WO<sub>3</sub> were observed for the Wa-series catalysts supported on chlorinated activated carbons (H1Wa and H2Wa), demonstrating that three-dimensional particles of tungsten oxide were formed in both catalysts.

The CO and CO<sub>2</sub> evolved up to 1273 K from the wet air pretreated supports and supported catalysts are listed in Table 4. It has been reported<sup>15</sup> that tungsten oxide supported on carbon can be reduced by the support at around 1130 K, producing CO. Furthermore, the reduction process is favored by the dispersion of the catalyst. After air pretreatments at 623 K, the amounts of CO and CO<sub>2</sub> evolved from supported catalysts were greater than those evolved from the support, because of the fixation of oxygen surface complexes on the carbon support



**Figure 2.** XRD patterns of supported catalysts pretreated in wet air at 623 K for 6 h.

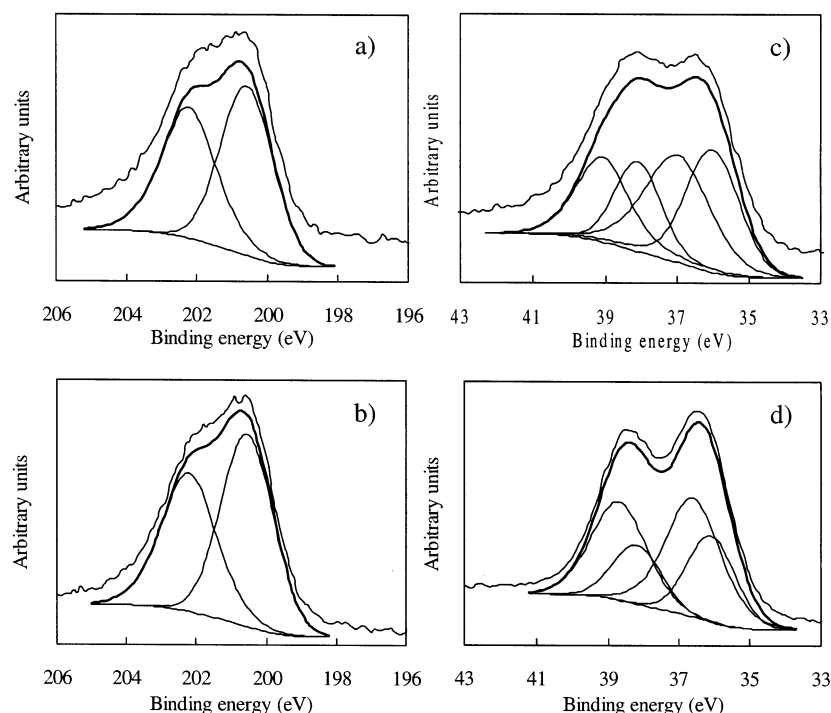
during the pretreatments. This occurs because tungsten oxide particles can dissociatively chemisorb oxygen from the air. The subsequent migration of the oxygen to the support yields oxygen surface complexes at the tungsten oxide–carbon interface that thermally evolve as CO and CO<sub>2</sub>. This process directly depends on the dispersion of the metal oxide phase. In addition, the amount of CO desorbed, which derives from the reduction of the tungsten oxide by the support, is also related to the dispersion. Therefore, a parameter  $Q$ , closely related to the dispersion of the tungsten oxide, is included in Table 4 and can be defined as

$$Q (\mu\text{mol}_{\text{oxygen}} \text{g}^{-1}) = [\text{CO}_{\text{CAT}} - \text{CO}_{\text{SUP}}] + 2[\text{CO}_2_{\text{CAT}} - \text{CO}_2_{\text{SUP}}]$$

The amounts of both CO and CO<sub>2</sub> evolved from the We series of supported catalysts were greater than those from the corresponding supports, whereas only the amount of CO evolved was greater in the case of the Wa series. Therefore, oxygen chemisorption that fixed CO<sub>2</sub>-evolving surface complexes occurred during air pretreatment only in the We series, indicating the greater dispersion of these catalysts, which is also shown by their much higher  $Q$  value. These results are in accordance with those obtained by XRD and HRTEM. Moreover, the value of  $Q$ , or the dispersion of the supported catalysts, markedly increased with the chlorine content of the support in the We series of catalysts, whereas this effect of chlorine was not observed in the Wa series.

XPS of the catalysts supported on chlorinated activated carbons was carried out before and after their pretreatment in wet air at 623 K. Spectra were recorded at C<sub>1s</sub>, O<sub>1s</sub>, Cl<sub>2p</sub>, and W<sub>4f</sub> photoelectron peaks in all catalysts, and the N<sub>1s</sub> region was also recorded in the Wa series.

The spectra of Cl<sub>2p</sub> and W<sub>4f</sub> levels for catalysts H1Wa and H1We before wet air pretreatment are shown in Figure 3a–d



**Figure 3.** Curve-fitted  $\text{Cl}_{2p}$  (a, b) and  $\text{W}_{4f}$  (c, d) core-level spectra for catalysts H1Wa (a, c) and H1We (b, d) before pretreatment in wet air.

**TABLE 5: Binding Energy Values (eV) of the  $\text{W}_{4f_{7/2}}$ ,  $\text{O}_{1s}$ , and  $\text{Cl}_{2p_{3/2}}$  Core-Level Spectra for Supports and Supported Catalysts from Series We before Pretreatment in Wet Air**

sample	$\text{W}_{4f_{7/2}}$	$\text{O}_{1s}$	$\text{Cl}_{2p_{3/2}}$	fwhm $\text{Cl}_{2p_{3/2}}$
H1		532.0 533.9	200.5	1.5
H1We	36.1 36.6	531.4 533.0	200.6	1.8
H2		531.9 533.9	200.5	1.5
H2We	35.9 36.6	531.2 533.0	200.5	1.8

as an illustration, including the curve-fitted spectra. The binding energies (BEs) of  $\text{O}_{1s}$ ,  $\text{Cl}_{2p_{3/2}}$ , and  $\text{W}_{4f_{7/2}}$  obtained from spectra similar to the above are compiled in Table 5. The  $\text{O}_{1s}$  core-level spectra of the supports showed two components: a peak at 532.0 eV, assigned to  $\text{C}=\text{O}$  double bonds from ketones and carboxylic acids; and a peak at 533.9, assigned to  $\text{C}-\text{O}$  single bonds.<sup>20</sup> Both peaks shifted to a lower BE for the supported catalysts, and the peak at 531.4 eV was assigned to both  $\text{C}=\text{O}$  double bonds and  $\text{W}-\text{O}$  bonds, because it has been described as corresponding to both  $\text{WO}_3$ -free<sup>15,21</sup> and  $\text{WO}_3$  monocrystals supported on  $\text{SiO}_2$ .<sup>22,23</sup>

The BE of  $\text{Cl}_{2p}$  at around 200.5 eV was the same in the supports as in their supported catalysts. However, the full width at half-maximum (fwhm) was wider in the supported catalysts than in their supports (see Table 5), which indicates some chlorine–tungsten interactions.

In the case of the We-series catalysts before wet air pretreatment, the  $\text{W}_{4f_{7/2}}$  core-level spectra showed two components at 36.1 and 36.6 eV, corresponding to tungsten(VI) surrounded by oxide ions and to the presence of  $\text{W}-\text{Cl}$  bonds, respectively. Thus, it has been shown<sup>24</sup> that tungsten oxychloride,  $\text{WOCl}_4$ , has a BE about 0.6 eV higher than that obtained for  $\text{WO}_3$  under the same conditions. Table 6 shows the atomic and mass ratios obtained from the spectra of the We series. Thus,  $(\text{W}^{\text{Cl}}/\text{W}_T)$  at indicates the ratio of the number of tungsten atoms bonded to surface chlorine to the total tungsten atoms. This ratio

**TABLE 6: Quantitative Results from XPS of Catalysts from Series We before Pretreatment in Wet Air**

catalyst	$(\text{W}^{\text{Cl}}/\text{W}_T)_{\text{at}}$	% $\text{W}_{\text{XPS}}$	% $\text{W}_{\text{XPS}}/\%$ $\text{W}_{\text{total}}$
H1We	0.638	26.81	3.6
H2We	0.622	28.68	3.7

**TABLE 7: Binding Energy Values (eV) of the  $\text{W}_{4f_{7/2}}$ ,  $\text{O}_{1s}$ ,  $\text{Cl}_{2p_{3/2}}$ , and  $\text{N}_{1s}$  Core-Level Spectra for Supports and Supported Catalysts from Series Wa before Pretreatment in Wet Air**

sample	$\text{W}_{4f_{7/2}}$	$\text{O}_{1s}$	$\text{Cl}_{2p_{3/2}}$	$\text{N}_{1s}$
H1		532.0 533.9	200.5	
H1Wa	36.0 37.0	531.5 533.5	200.6	400.3 (24) <sup>a</sup> 402.7 (76)
H2		531.9 533.9	200.5	
H2Wa	36.1 36.9	531.6 533.5	200.6	399.5 (21) 402.6 (79)

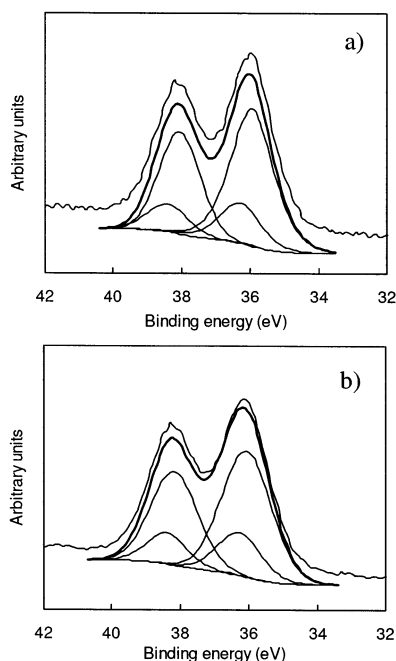
<sup>a</sup> Percentage of nitrogen complexes.

is similar and relatively high in both catalysts, indicating that a high proportion of tungsten oxide is anchored to the supports through their chlorine surface complexes during their preparation. It is important to point out that tungsten pentaethoxide was not detected in these catalysts. The reactivity of this compound to humidity is very high, and the ambient humidity probably hydrolyzed the tungsten–ethoxide bonds.<sup>25</sup>

The ratio between the number of tungsten atoms determined by XPS and the total number of tungsten atoms determined by chemical analysis ( $\% \text{W}_{\text{XPS}}/\% \text{W}_{\text{total}}$ ) is given in Table 6. This ratio was similar in both catalysts, and its high value indicates that there is a high proportion of tungsten on the more external surface of the carbon particles.

In the case of Wa-series catalysts before wet air pretreatment, Table 7 shows the binding energy values of  $\text{N}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{Cl}_{2p_{3/2}}$ , and  $\text{W}_{4f_{7/2}}$ , and Table 8 displays the atomic and mass ratios obtained from the spectra. The  $\text{O}_{1s}$  and  $\text{Cl}_{2p}$  core-level spectra showed the same components as found in the We series.





**Figure 4.** Curve-fitted  $W_{4f}$  core-level spectra for catalysts H1Wa (a) and H1We (b) pretreated in wet air at 623 K for 6 h.

**TABLE 8: Quantitative Results from XPS of Catalysts from Series Wa before Pretreatment in Wet Air**

catalyst	$(N_{NH_4^+}/W_T)_{at}$	$(W^{NH_4^+}/W_T)_{at}$	% $W_{XPS}$	% $N_{XPS}$	% $W_{XPS}/W_{total}$
H1Wa	1.043	0.523	24.27	2.54	3.3
H2Wa	1.074	0.593	28.75	2.98	3.6

However,  $W_{4f_{7/2}}$  showed two components at around 36.0 and 37.0 eV, which have been assigned to W(VI) in tungsten oxide and ammonium tungstate,<sup>19</sup> respectively. The presence of ammonium tungstate in the catalysts is revealed by a peak in the  $N_{1s}$  region at 402.6 eV, which corresponds to  $NH_4^+$  ions. Furthermore, the ratio between nitrogen atoms in ammonia ions and total tungsten atoms was double that between tungsten atoms in ammonium tungstate and total tungsten atoms (see Table 8). These catalysts showed about 20% of the nitrogen as amino groups (BE at around 400 eV), probably bound to the support.

Finally, the values of the %  $W_{XPS}/W_{total}$  ratio were the same as those found in the catalysts from the We series.

XPS of the above catalysts was also carried out after their pretreatment in wet air at 623 K. XPS profiles of the  $W_{4f}$  level for catalysts H1Wa and H1We are depicted in Figure 4 as an example. The BE values of  $O_{1s}$ ,  $Cl_{2p_{3/2}}$ , and  $W_{4f_{7/2}}$  are compiled in Table 9. The  $O_{1s}$  and  $Cl_{2p}$  core-level spectra showed the same component as before. The  $W_{4f_{7/2}}$  showed two components at around 36.0 and 36.3–36.5 eV, which are assigned to W(VI) bound to oxygen in the tungsten oxide and to W(VI) bound to the chlorine surface complexes, respectively. Therefore, in the Wa-series catalysts the W–Cl bonds are formed during the pretreatment in wet air of the fresh catalysts. After the pretreatment, all ammonium tungstate was decomposed, and there was no evidence of ammonium ions or amino groups in the  $N_{1s}$  region.

Atomic and mass ratios obtained from XP spectra are compiled in Table 10. If the %  $W_{XPS}/W_{total}$  ratios before and after the pretreatment of the catalyst are compared, it is observed that this ratio did not change in the We-series catalysts (Tables 6 and 10). However, in the Wa-series catalysts (Tables 8 and 10) this ratio largely decreased after pretreatment. It was

**TABLE 9: Binding Energy Values (eV) of the  $O_{1s}$ ,  $W_{4f_{7/2}}$ , and  $Cl_{2p_{3/2}}$  Core-Level Spectra for Catalysts Pretreated in Wet Air at 623 K for 6 h**

catalyst	$O_{1s}$	$W_{4f_{7/2}}$	$Cl_{2p_{3/2}}$
HWe	531.3 533.6	35.9	-
H1We	531.5 533.6	36.0 36.3	200.5
H2We	531.4 533.5	36.0 36.5	200.4
HWa	531.3 533.6	36.0	-
H1Wa	531.4 533.6	35.9 36.3	200.5
H2Wa	531.4 533.7	35.8 36.3	200.4

**TABLE 10: Quantitative Results from XPS of Catalysts after Pretreatment in Wet Air at 623 K for 6 h**

catalyst	$(W^{Cl}/W_T)_{at}$	% $W_{XPS}$	% $W_{total}$	% $W_{XPS}/W_{total}$
HWe		17.79	6.9	2.6
H1We	0.229	22.51	7.5	3.0
H2We	0.302	25.30	7.7	3.3
HWa		15.10	7.4	2.0
H1Wa	0.214	13.37	7.4	1.8
H2Wa	0.298	10.61	8.1	1.3

commented above that in the We series, the W–Cl bonds were formed during the preparation of the supported catalysts and that there was no evidence of the presence of tungsten pentaethoxide. Therefore, during the pretreatment in wet air of these supported catalysts there was no redistribution of the metal oxide phase, because the %  $W_{XPS}/W_{total}$  ratio remained unchanged with the pretreatment. However, the proportion of tungsten bound to chlorine surface complexes drastically diminished with the pretreatment, as indicated by  $(W^{Cl}/W_T)_{at}$  ratio given in Tables 6 and 10. This is because the humidity present in the atmosphere of the pretreatment partially hydrolyzed the W–Cl bonds. Thus, the XPS studies showed a larger number of W–Cl bonds in the catalysts after the pretreatment in dry air. Therefore, the number of these W–Cl bonds that remain after pretreatment should be those in equilibrium at the water vapor pressure used in the wet air flow.

In the case of the Wa-series catalysts, the pretreatment produced the decomposition of ammonium tungstate, which was essentially located at the more external surface of the carbon particles and, in addition, gives rise to the formation of W–Cl. Both processes produce a redistribution of the metal oxide phase that markedly decreases the %  $W_{XPS}/W_{total}$  ratio with the pretreatment. According to the XRD results, these catalysts contain large three-dimensional crystals of tungsten oxide after the wet air pretreatment. This would explain the decrease in the above mass ratio, because the formation of large three-dimensional particles instead of laminar particles, as in the case of the We-series catalysts, would mean that a smaller number of tungsten surface atoms could be detected by XPS. Finally, the proportion of tungsten bound to chlorine surface complexes is the same as that found for the corresponding We-series catalysts.

## Conclusions

The results of the present study clearly show that tungsten oxide is partially anchored to the chlorine surface complexes of the carbon support through the formation of W–Cl bonds. This was produced during the preparation of the We-series supported catalysts and during the wet air pretreatment of the Wa series. In both series of catalysts, the tungsten oxide phase

is essentially located on the more external surface of the carbon particles either as large three-dimensional crystals (Wa series) or as thin films with very low crystallinity (We series). During the pretreatment in wet air, the metal oxide phase was redistributed in Wa-series catalysts, whereas this redistribution did not take place in the We series because the precursor was decomposed and partially anchored to the support during the preparation of the supported catalysts. Finally, the We-series catalysts had the highest dispersion, which increased with higher chlorine content of the support.

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