Surface Characteristics of Titania/Carbon Composite Aerogels

C. Moreno-Castilla,*† F. J. Maldonado-Hódar,‡ F. Carrasco-Marín,† and Enrique Rodríguez-Castellón‡

Grupo de Investigación en Carbones, Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain, and Departamento de Química Inorgánica, Universidad de Málaga, Málaga, Spain

Received October 25, 2001. In Final Form: December 17, 2001

Titania/carbon composite aerogels with a nominal titania content between 10 and 50% were prepared by the sol–gel method. The samples obtained were heat treated at 500 and 900 °C in He flow. All composite aerogels and their carbonized derivatives were characterized by physical adsorption and mercury porosimetry to determine their surface area and pore texture. The surface chemistry was studied by X-ray diffraction, X-ray photoelectron spectroscopy, and temperature-programmed desorption of ammonia previously adsorbed at 100 °C. Results showed that development of the meso- and macroporosity as well as the surface area depended on the titania content and the heat treatment. The titania phase in the composite aerogels was uniformly and well dispersed up to a real titania content of around 70%, either as anatase or as a mixture of anatase and rutile. The surface acid sites of the metal oxide phase were of the Lewis type, and it was well dispersed up to the above titania content. In the composites with higher titania content there was a sintering of the metal oxide particles, which increased with temperature.

Introduction

The sol–gel technique is an excellent method to prepare metal oxide/carbon composite aerogels and xerogels, which permit dispersion of the metal oxide nanoparticles into the porosity of the carbon matrix.1–6 The importance of the supercritical drying, in the preparation of titania/carbon composite aerogels, to obtain a composite with a well-developed mesoporosity into which the titania nanoparticles are well dispersed has been demonstrated recently.5

Titania, in its crystallographic form of anatase, has been found to be the best photocatalyst to purify polluted water.7 Its efficiency increases when supported on activated carbon,1–13 because it acts as a coadsorbent with a better-developed surface area and porosity than the metal oxide. More recently,11,12 it has been shown that physical mixtures of titania and activated carbons have a synergic effect for the photodegradation of phenol and other model compounds.

* Corresponding author. E-mail: cmoreno@ugr.es
† Universidad de Granada.
‡ Universidad de Málaga.

(1) Maldonado-Hódar, F. J.; Ferro-García, M. A.; Rivera-Utrilla, J.; Moreno-Castilla, C. Carbon 1999, 37, 1199.

On the other hand, titania/carbon composite catalysts have been used recently9 in the aromatization reaction of n-octane with a high selectivity. These authors also found a degree of cooperation between the metal oxide phase and the carbon matrix, which resulted in an increased dehydrogenation activity.

According to these references, titania/carbon catalysts can present synergistic or cooperation effects between the metal oxide and the carbon phase. It is expected that this effect would be enhanced if the metal oxide particles were well dispersed on the carbon phase. This can be achieved by the sol–gel method of catalyst preparation.5 The titania/carbon catalysts can be used, depending on their applications, with very different titania content. Thus, the objective of this work is to study the change in pore texture, surface chemistry, and metal oxide dispersion of several titania/carbon composite aerogels with different titania content.

Experimental Section

Four titania/carbon composite aerogels were prepared by using an initial solution containing 6.18 g of resorcinol and 9.08 g of formaldehyde (37 wt %) in 8.35 g of water. No acid catalyst was added for the polymerization because this solution had a pH close to 3. Tetrabutyl orthotitanate (TBTi) dissolved in cyclohexane was added drop by drop to the above solution, which was kept at 60–70 °C under reflux with vigorous and continuous stirring. The amount of TBTi was calculated to obtain a nominal TiO2 content in the aerogel of 10, 20, 30, and 50 wt %. The resulting gel was aged for 1 h at 60–70 °C. The solid was further dried overnight at 80 °C and dried in supercritical CO2. The aerogels obtained will be referred to as their nominal TiO2 content.

The titania/carbon composite aerogels were carbonized by heating to 500 or 900 °C in N2 flow, 100 cm3/min, with a heating rate of 10 K/min and a soaking time of 1.5 h. These samples will be referred to in the text by adding the carbonization temperature to the aerogel name. The real TiO2 content of all samples was obtained by burning off an aliquot part at 900 °C until constant weight. The oxide samples obtained were used later as reference material.

Textural characteristics of all samples were obtained by CO₂ adsorption at 0 °C and mercury porosimetry up to 4200 cm³/gm², by using a Quantachrome Autoscan 60 porosimeter. The Dubinin–Radushkevich equation was applied to the CO₂ adsorption isotherm from which the micropore volume, \( V_\text{B} \), was obtained. The apparent surface area accessible to CO₂ (SCO₂) was obtained from \( W_0 \) by assuming a liquid density of 1.03 gm/cm³ and a molecular area of 0.187 nm² for CO₂ at 0 °C (3,14,15).

From mercury porosimetry experiments the following parameters were obtained: pore size distribution, PSD, of pores with a diameter wider than 3.7 nm; the surface area of these pores, which will be referred to as external surface area, \( S_\text{ext} \); pore volume corresponding to pores with a width between 3.7 and 50 nm, \( V_2 \), or mesopore volume, although in fact the mesopore volume is between 2 and 50 nm; \( V_3 \), pore volume of pores with a diameter larger than 50 nm, or macropore volume, \( V_0 \); particle density, \( \rho \).

X-ray diffraction, XRD, was carried out with a Phillips PW 1710 diffractometer (40 kV and 40mA) using Cu Kα radiation.

X-ray photoelectron spectroscopy, XPS, measurements were carried out with a Physical Electronic 5700 equipment with Mg Kα X-ray excitation source (hv = 1253.6 eV) and hemispherical electron analyzer. Accurate (0.1 eV) binding energies were determined with respect to the position of the C1s peak at 284.8 eV. The atomic concentrations were calculated from photoelectron peak areas, using Shirley background subtraction \(^1^9\) and sensitivity factors provided by the spectrometer manufacturer PHI.\(^{20}\)

Total surface acidity of carbonized composite aerogels was determined by temperature-programmed desorption (TPD) of previously adsorbed NH₃. For this purpose, the samples were heated in He flow (30 cm³/min for 30 min) at 400 °C for 30 min and then they were cooled to 100 °C and the He flow switched to NH₃ flow at a rate of 30 cm³/min for 30 min. After this, NH₃ flow was switched again to He for 30 min, to remove the physisorbed NH₃. For this purpose, the samples were introduced in the analysis chamber without any contact with the atmosphere. The residual pressure in the analysis chamber was maintained below 10⁻⁹ Torr during data acquisition. Survey and multiregion spectra were recorded at TTP(300, 150, and 1253.6 eV) and C1s photoelectron peaks. Each spectral region of interest was scanned several times and the obtained good signal-to-noise ratios. The atomic concentrations were calculated from photoelectron peak areas, using Shirley background subtraction \(^1^9\) and sensitivity factors provided by the spectrometer manufacturer PHI.\(^{20}\)

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### Results and Discussion

The real TiO₂ content and surface characteristics of the samples are compiled in Table 1. In this table, samples A-1000 and TiO₂ are also included for comparison. A-1000 is a carbonized aerogel obtained at 1000 °C that has been studied elsewhere.\(^2\) Sample TiO₂ is the resulting residue from a titania/carbon composite aerogel as a result of its carbonization and consequent weight loss.

In the case of the titania/carbon composite aerogels the micro-, meso-, and macro pore volumes, \( V_0 \), \( V_2 \), and \( V_3 \), respectively, reached their higher values for samples 20 and 30. Thus, samples 20 and 30 are essentially meso- and macroporous.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO₂ content (%)</th>
<th>( \rho ) (g/cm³)</th>
<th>( V_3 ) (cm³/g)</th>
<th>( V_2 ) (cm³/g)</th>
<th>( W_0 ) (cm³/g)</th>
<th>( S_\text{ext} ) (m²/g)</th>
<th>( S_\text{CO₂} ) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>14</td>
<td>0.72</td>
<td>0.491</td>
<td>0.112</td>
<td>0.057</td>
<td>37</td>
<td>149</td>
</tr>
<tr>
<td>10/500</td>
<td>24</td>
<td>0.73</td>
<td>0.490</td>
<td>0.126</td>
<td>0.175</td>
<td>33</td>
<td>461</td>
</tr>
<tr>
<td>10/900</td>
<td>27</td>
<td>0.81</td>
<td>0.431</td>
<td>0.072</td>
<td>0.266</td>
<td>25</td>
<td>700</td>
</tr>
<tr>
<td>20</td>
<td>22</td>
<td>0.52</td>
<td>0.619</td>
<td>0.443</td>
<td>0.075</td>
<td>128</td>
<td>195</td>
</tr>
<tr>
<td>20/500</td>
<td>37</td>
<td>0.65</td>
<td>0.374</td>
<td>0.309</td>
<td>0.133</td>
<td>74</td>
<td>350</td>
</tr>
<tr>
<td>20/900</td>
<td>41</td>
<td>0.71</td>
<td>0.404</td>
<td>0.309</td>
<td>0.157</td>
<td>68</td>
<td>415</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>0.54</td>
<td>0.688</td>
<td>0.411</td>
<td>0.061</td>
<td>137</td>
<td>161</td>
</tr>
<tr>
<td>30/500</td>
<td>46</td>
<td>0.68</td>
<td>0.465</td>
<td>0.344</td>
<td>0.073</td>
<td>102</td>
<td>191</td>
</tr>
<tr>
<td>30/900</td>
<td>54</td>
<td>0.67</td>
<td>0.519</td>
<td>0.380</td>
<td>0.163</td>
<td>101</td>
<td>429</td>
</tr>
<tr>
<td>50</td>
<td>49</td>
<td>1.19</td>
<td>0.040</td>
<td>0.133</td>
<td>0.049</td>
<td>63</td>
<td>128</td>
</tr>
<tr>
<td>50/500</td>
<td>73</td>
<td>1.70</td>
<td>0.042</td>
<td>0.047</td>
<td>0.054</td>
<td>14</td>
<td>142</td>
</tr>
<tr>
<td>50/900</td>
<td>84</td>
<td>1.64</td>
<td>0.052</td>
<td>0.069</td>
<td>0.070</td>
<td>20</td>
<td>184</td>
</tr>
<tr>
<td>A-1000</td>
<td>0</td>
<td>0.72</td>
<td>0.628</td>
<td>0.000</td>
<td>18</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>100</td>
<td>1.60</td>
<td>0.246</td>
<td>0.000</td>
<td>2</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

The PSD for samples from series 10, 20, and 30 are depicted in Figure 1, and they show that (i) their shape practically did not change with carbonization of the composite aerogel at both 500 and 900 °C and (ii) the PSD of samples from series 10 is unimodal, with a maximum centered at around a diameter of 60 nm, whereas for samples from series 20 and 30 the PSD is bimodal, with maxima centered at around 25 nm and 2000 nm.

XRD patterns of all composite aerogels and of the carbonized derivatives from series 10, 20, and 30 did not have any diffraction peak corresponding to the inorganic phase. However, the XRD patterns of samples 50/500 and 50/900, depicted in Figure 2, show the diffraction peaks of anatase and a mixture of anatase and rutile, respectively. Anatase is a metastable polymorphic form of titania at all temperatures and transforms to rutile upon heating.

After purging the transformation is very rapid at temperatures above 730 °C,\(^2\) but the phase transition to rutile occurs at all temperatures and transforms to rutile upon heating.

The main diffraction peaks, (101) for anatase and (110) for rutile, are of particular importance in samples 20 and 30 and their respective carbonized derivatives. Similarly, the TiO₂ sample has no mesopores and a smaller macropore volume than samples from series 10, 20, and 30.

(20) Physical Electronics, 6509 Flying Cloud Drive, Eden Prairie, Mn 55344.
When the carbonized derivatives obtained at 500 °C were burned in air, the residue left was identified as a mixture of anatase and rutile, whereas samples carbonized at 900 °C left a residue of rutile, as shown in Figure 2. The XRD patterns of these oxides showed narrow diffraction peaks reflecting that, during burnoff of the carbonaceous phase, the TiO₂ particles were sintered. These results imply that the carbon matrix prevents the sintering of titania nanoparticles and in some manner stabilizes the anatase polymorphic form.

XPS patterns of the Ti 2p and O 1s core-level of sample 30/500 are shown in Figure 3 as an example. The binding energy of the Ti 2p₃/2 and the surface atomic ratio, (Ti/C)ₛ, are compiled in Table 2. The O 1s core level spectra of the carbonized composite aerogels showed four components at 530.8 ± 0.2, 532.4 ± 0.2, 533.7 ± 0.1, and 535.4 ± 0.3 eV. The percentages of these four peaks as well as the surface atomic ratio (O/C)ₛ are compiled in Table 3. These results indicate that in the carbonized composite aerogels titanium was in oxidation state IV, with a BE value at 459.2 ± 0.1 eV, except in the case of the sample with the higher Ti content, 50/900, which is shifted to 459.6 eV.

Information about supported metal particles can be obtained from the metal/support atomic ratios.²²,²³ Thus, Figure 4 shows the relationship between the surface atomic ratio, (Ti/C)ₛ, and the total or bulk atomic ratio, (Ti/C)ₜ, for all the carbonized composite aerogels. The linear relationship found between the two magnitudes, except for sample 50/900, indicates that the TiO₂ phase is uniformly dispersed in the composite up to a total TiO₂ content of 73%. The deviation of sample 50/900 from the straight line is due to its higher TiO₂ content, which allows the increase of metal oxide particles by sintering and, consequently, produces a drop in the amount of Ti detected by XPS.

with the TiO2 content of the carbonized composite aerogel quinone groups.25

The relationship between the surface atomic ratios (O/C) and Ti/C surface atomic ratios is shown in Figure 5. Two parallel straight lines were obtained, one for each series of carbonized composite aerogels. The slope of both straight lines is close to 2 (2.6 and 2.4 for 500 and 900 series, respectively). The separation between them corresponds to the different oxygen content of the carbon phase.

The O1s core-level spectra showed four components. The peak at 530.8 ± 0.2 eV is due to both Ti-O bonds in the TiO2 phase24 and to C=O bonds in quinones and anhydrides25 and the second one, at 533.7 ± 0.1 eV, to C-O bonds in ethers and anhydrides and oxygen atoms in carboxyl groups. The stability of these surface groups decreases with the increase in heat treatment temperature, and the composite aerogels carbonized at 900 °C, therefore, show a lower intensity for these peaks, especially for the second one. As a logical consequence of the rise in TiO2 content in the carbonized composite aerogels, the intensity of these peaks decreases. Finally, the peak at 535.4 ± 0.2 eV is due to chemisorbed water.25

The acid–base surface characteristics of the carbonized composite aerogels were studied by TPD of ammonia previously adsorbed at 100 °C. In general, it is accepted that NH3 is an excellent molecular probe to measure total surface acidity since; due to its strong basicity and small molecular size, it allows the measurement of acidic surface sites in narrow pores.28–32 The ammonia desorption profiles obtained with samples 30/500 and 30/900 are depicted in Figure 6, as an example. The desorption profiles were obtained up to the carbonization temperature of the samples. Measurements of total surface acidity were obtained from the area under these profiles and are recorded in Table 4. The amounts of ammonia desorbed, shown in this table, are given per gram of TiO2, since the carbonaceous phase of the composite should chemisorb no ammonia at the experimental conditions used. This was checked with the blank sample A-1000.

Acid sites on solid surfaces can be of the Brønsted and Lewis type depending on the nature of the solid.33 The acid-base surface characteristics of the carbonized composite aerogels can be studied by TPD of ammonia previously adsorbed at 100 °C. In general, it is accepted that NH3 is an excellent molecular probe to measure total surface acidity since; due to its strong basicity and small molecular size, it allows the measurement of acidic surface sites in narrow pores.28–32 The ammonia desorption profiles obtained with samples 30/500 and 30/900 are depicted in Figure 6, as an example. The desorption profiles were obtained up to the carbonization temperature of the samples. Measurements of total surface acidity were obtained from the area under these profiles and are recorded in Table 4. The amounts of ammonia desorbed, shown in this table, are given per gram of TiO2, since the carbonaceous phase of the composite should chemisorb no ammonia at the experimental conditions used. This was checked with the blank sample A-1000.

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Titania/Carbon Composite Aerogels

Table 4. Amount of NH\textsubscript{3} Desorbed from the Titania/Carbon Composite Aerogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH\textsubscript{3} desorbed up to 500 °C (μmol/g of TiO\textsubscript{2})</th>
<th>NH\textsubscript{3} desorbed up to 900 °C (μmol/g of TiO\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/500</td>
<td>713</td>
<td>900</td>
</tr>
<tr>
<td>20/500</td>
<td>697</td>
<td>900</td>
</tr>
<tr>
<td>30/500</td>
<td>693</td>
<td>900</td>
</tr>
<tr>
<td>50/500</td>
<td>436</td>
<td>622</td>
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<tr>
<td>10/900</td>
<td>563</td>
<td>622</td>
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<tr>
<td>20/900</td>
<td>539</td>
<td>580</td>
</tr>
<tr>
<td>30/900</td>
<td>561</td>
<td>601</td>
</tr>
<tr>
<td>50/900</td>
<td>165</td>
<td>173</td>
</tr>
</tbody>
</table>

with a hydroxylated surface) and after heating at 800 °C in air (a pure rutile with a nearly completely dehydroxylated surface) the surface acid sites were of the Lewis type, and the different surface hydroxyl groups showed no Brønsted activity (against pyridine). Furthermore, it was found\textsuperscript{35} by adsorption microcalorimetry of ammonia on bulk titania that the ammonia molecules were coordinatively bonded to titanium atoms and that two types of Lewis acid sites were present on the titania surface. Partial dissociation of the ammonia adsorbed was also observed.

Results given in Table 4 indicate, first, that, for carbonized composite aerogels obtained at 900 °C, more than 90% of ammonia is desorbed up to 500 °C. Second, samples 10/500, 20/500, and 30/500 show the same total surface acidity; similarly this occurs with samples 10/900, 20/900, and 30/900, although their values are lower than in the series of samples carbonized at 500 °C. This indicates that in both series of samples the surface acid sites are uniformly dispersed and linearly increase with the titania content as shown by XPS measurements.

The slight decrease in the number of surface acid sites when the carbonization temperature of aerogels 10, 20, and 30 increased is associated with the nature of their surface acid sites. Thus, if the surface –OH groups (Brønsted type) do not contribute to the total surface acidity, their loss by heat treatment at 900 °C would practically not affect the total surface acidity. The explanation for these results lies in the fact that the surface acid sites of these samples are of the Lewis type. This kind of surface acid site is hardly affected by the increase in treatment temperature from 500 to 900 °C because, as shown by XPS, the titania phase did not change its chemical composition. This is expected because, from a thermodynamic viewpoint,\textsuperscript{36} carbon cannot reduce titania in the above temperature range. Therefore, the slight change in surface acidity found could be related to the change in the anatase/rutile ratio with temperature, due to the different populations of coordinatively unsaturated Ti cations on the surface of the two polymorphs.\textsuperscript{37}

Finally, sample 50/500 shows the lowest surface acidity within its series because, due to its high titania content, it has the largest particle size. When the heat treatment was increased up to 900 °C, sample 50/900, there was a large decrease in surface acidity due to sintering of the TiO\textsubscript{2} particles. Thus, for a titania content in the aerogel higher than about 70% the carbon matrix cannot prevent sintering of the oxide particles. The increase in treatment temperature largely increases sintering of the titania particles because the Tamman temperature\textsuperscript{38} of titania (rutile) is around 780 °C.

Conclusions

Our results indicate that the meso- and macroporosity of the original composite aerogels increases up to a titania content of 30%. Especially original composite aerogels containing 20 and 30% of titania and their carbonized derivatives have a well-developed meso- and macroporosity with a bimodal pore size distribution. Surface areas are in the 200–700 m\textsupersq/m range.

XRD experiments show that, for composite aerogels containing up to around 55% of titania, the metal oxide phase is well dispersed with a crystal size smaller than 4 nm, either essentially as anatase in samples prepared at 500 °C or as a mixture of anatase and rutile in those prepared at 900 °C. The metal oxide phase was uniformly dispersed up to a titania content in the composite aerogel of around 70%, as deduced from XPS experiments. These also showed that titanium was in oxidation state IV, even after heating at 900 °C in He flow. This is expected from a thermodynamic viewpoint.

Surface acid sites on the metal oxide phase in the composite aerogel, which seem to be of the Lewis type, are well-dispersed and uniformly distributed up to a titania content of 70%. Above this, the carbon matrix cannot prevent sintering of the metal oxide phase, which largely increases when the treatment temperature increases from 500 up to 900 °C.

Acknowledgment. The authors wish to acknowledge the DGESIC for financial support, Project No. PB97-0831. LA011595U


