

Influence of Carbon–Chlorine Surface Complexes on the Properties of Tungsten Oxide Supported on Activated Carbons. 2. Surface Acidity and Skeletal Isomerization of 1-Butene

Francisco J. Maldonado-Hódar,[†] Agustín F. Pérez-Cadenas,[†] J. L. G. Fierro,[‡] and Carlos Moreno-Castilla^{*,†}

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain, and Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

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Chlorinated activated carbons and the respective tungsten oxide catalysts supported on them were tested as catalysts in the decomposition reaction of 2-propanol and characterized by measurement of their pH_{PZC} . Supported catalysts were also used in the skeletal isomerization of 1-butene. Results found show that an increase in the chlorine content of the support increases the total surface acidity, as measured by the pH_{PZC} , of both the support and the supported catalysts. However, there is also a decrease in their Brönsted type acidity, as determined from the results obtained from the dehydration reaction of 2-propanol. Thus, it seems that the effect of chlorine is to increase Lewis type acidity in both the support and the supported catalyst. In addition, during the dehydration of 2-propanol there was a partial reduction of W(VI) to W(V) in most of the catalysts, which brought about a restructuring of the metal oxide particles. Isomerization of 1-butene gives only isobutene and *trans*-2-butene. Selectivity to obtain isobutene decreases when the reaction temperature and total conversion increases. Activity to obtain isobutene shows the same trend as the dehydration of 2-propanol and decreases when the chlorine content of the support increases.

Introduction

Solids with acidic character have applications as catalysts in many reactions of great industrial importance, including those involving hydrocarbon conversions such as polymerization, isomerization, methathesis, cracking, and re-forming.^{1–3} In these reactions, the surface active sites are of Brönsted acid type.

Metal oxides of many transition elements are among the acidic solids used as catalysts. Out of all of these, those with the metal in oxidation state five or six have the stronger Brönsted acid sites. Furthermore, in these cases there are $\text{M}=\text{O}$ double bonds in the oxides, which allow the delocalization of the ionic charge resulting from the donation of protons, with the consequent stabilization of the conjugated base of the oxide.⁴ Metal oxides with these characteristics are vanadium and niobium pentoxide and molybdenum and tungsten trioxide. Among these, tungsten oxide has the strongest Brönsted acid sites, either as a bulk metal oxide^{4–6} or supported on SiO_2 ,⁴ Al_2O_3 ,^{7–10} TiO_2 ,^{4,11} or ZrO_2 .^{12–16}

In addition, Bernholc et al.⁷ demonstrated by theoretical calculations that an additional increase in the surface acidity of the metal oxide occurs if the delocalization of the negative charge in the oxide is extended to the support. Therefore, the stabilization of the negative charge of the metal oxide occurs by its delocalization among the terminal oxygen atoms, the metal atoms, and the support. This suggests that the surface chemistry of carbons can have a major influence on the surface acidity of tungsten oxide supported catalysts.

Our laboratory previously used tungsten oxide supported on activated carbons for the skeletal isomerization of 1-butene¹⁷

and the dehydration of alcohols.¹⁸ The results suggested that the support, of basic character ($\text{pH}_{\text{PZC}} = 10.2$), moderates the acid strength of the tungsten oxide, especially for catalysts with low tungsten loading.

In the first part of the present work¹⁹ we described the effect of the chlorine content of activated carbons on the dispersion, distribution, and chemical nature of the metal oxide phase. It is known that chlorine surface complexes on activated carbons increase their surface acidity;^{20–22} therefore in this second part we analyze the effect of these complexes on the surface acidity of the supported catalysts and on the skeletal isomerization of 1-butene, a reaction that is related to the surface acidity of the catalyst.

Experimental Section

Preparation of activated carbon H and of chlorinated samples H1 and H2 was described in detail in the first part of this series.¹⁹ The catalysts were prepared as previously reported¹⁹ from two different precursors, ammonium tungstate and tungsten pentaethoxide. 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.

Surface acidity of the supports and supported catalysts was evaluated by studying the decomposition reactions of 2-propanol, using a plug-flow microreactor working at atmospheric pressure with He as carrier gas. The experimental procedure is described in detail elsewhere.²³ Prior to the catalytic activity measurements, the samples were pretreated at 623 K for 6 h in wet air.

Analysis of the reaction products was carried out by on-line gas chromatography. Propene and acetone were the main reaction products obtained. Very small amounts of diisopropyl ether were also detected in all cases. The activity to obtain a

* Corresponding author. Tel: 34-958-243323. Fax: 34-958-248526. E-mail: cmoreno@ugr.es.

[†] Universidad de Granada.

[‡] CSIC.

TABLE 1: pH_{PZC} and Oxygen and Chlorine Content of the Supports Pretreated in Wet Air at 623 K for 6 h

support	pH _{PZC}	% O _{TPD}	% O _{XPS}	% Cl _{XPS}	% Cl _{TOTAL}
H	7.81	4.84	5.37	-	0.0
H1	5.72	4.39	6.66	8.69	8.4
H2	5.49	4.57	6.47	11.58	11.0

given species, r_x , was calculated using

$$r_x = \frac{FC_x}{W} \quad (1)$$

where F is the 2-propanol flow through the catalyst in moles per min, C_x is the 2-propanol conversion to species x , and W is the weight (g) of the support or the tungsten in the supported catalyst. The reaction was carried out in the temperature range between 363 and 383 K to keep the total conversion below 10% and, so, to operate under differential conditions.

Surface acidity was also evaluated by measuring the pH of the point of zero charge (pH_{PZC}), following a method described elsewhere.²⁴ For this purpose, 0.25 g of sample was added to 4 mL of CO₂-free distilled water and the suspension so obtained was thermostated at 298 K, measuring the pH from time to time until it was stabilized.

The isomerization reaction of 1-butene was performed in the above experimental system using a He flow containing 1.6% of 1-butene. Products were analyzed by gas chromatography using a flame ionization detector and a GS-alumina capillary column (50 m × 0.53 mm) supplied by J&W Scientific. The experimental procedure was described in detail elsewhere.¹⁷

The activity to obtain a given species was calculated from eq 1 where F is now the 1-butene flow. This equation was applied, as in the above case, when the total conversion was below 10%.

Results and Discussion

Surface Acidity of the Supports. Table 1 exhibits the pH_{PZC} and oxygen and chlorine content of the supports after their pretreatment in wet air at 623 K, obtained by TPD and XPS. The total chlorine content was similar to Cl_{XPS}, indicating that this halogen was homogeneously distributed through the carbon particles. The O_{TPD} value was obtained from the amounts of CO and CO₂ evolved up to 1273 K and can be considered as the total oxygen content of the samples. The O_{TPD} for the chlorinated supports, H1 and H2, was slightly lower than for the original carbon H. This total oxygen content was always lower than the O_{XPS}, indicating that the oxygen surface complexes were primarily fixed on the more external surface of the carbon particles. Despite the slightly lower O_{TPD} for the chlorinated samples, they had a greater total surface acidity or lower pH_{PZC} than the original carbon H, and this acidity was greater with a higher chlorine content of the carbon.

Many catalytic reactions have been used to quantify the surface acidity of solids. Ai et al.^{25–30} proposed the use of the decomposition reaction of 2-propanol to indirectly determine this acid–base character. From a mechanistic standpoint, the dehydration of 2-propanol is catalyzed by the acid sites and its dehydrogenation by both acid and basic sites. Therefore, and according to the present authors, the dehydration rate is a measurement of the total surface acidity and the ratio between dehydrogenation and dehydration rates can be taken as a measurement of the total surface basicity.

After the pretreatment of the supports in wet air at 623 K, they were active in the decomposition reaction of 2-propanol in the temperature range between 403 and 443 K, and propene

TABLE 2: Activity To Obtain Propene, at 403 K, with the Supports after Their Pretreatment in Wet Air at 623 K for 6 h

sample	r_p ($\mu\text{mol g}^{-1} \text{min}^{-1}$)
H	4.3
H1	2.2
H2	1.6

TABLE 3: Results Obtained in the Decomposition Reaction of Isopropanol at 363 K with Catalysts from Series We and Their pH_{PZC} after Their Pretreatment in Wet Air at 623 K for 6 h

catalyst	C (%)	r_p ($\mu\text{mol g}^{-1} \text{min}^{-1}$)	r_A ($\mu\text{mol g}^{-1} \text{min}^{-1}$)	pH _{PZC}
HWe	8.3	109.1	9.9	3.6
H1We	5.9	81.8	11.9	3.1
H2We	5.0	56.7	9.6	2.7

TABLE 4: Results Obtained in the Decomposition Reaction of Isopropanol at 383 K with Catalysts from Series Wa and Their pH_{PZC} after Their Pretreatment in Wet Air at 623 K for 6 h

catalyst	C (%)	r_p ($\mu\text{mol g}^{-1} \text{min}^{-1}$)	r_A ($\mu\text{mol g}^{-1} \text{min}^{-1}$)	pH _{PZC}
HWa	8.1	134.8	16.2	4.4
H1Wa	3.9	52.6	6.0	4.4
H2Wa	2.6	25.7	3.3	4.5

was the only reaction product obtained, so that the activated carbons used can be considered as dehydration catalysts. According to our results, the propene formation rate (r_p) decreased when the chlorine content of the catalyst increased (Table 2). The dehydration of 2-propanol to propene is known to be catalyzed by Brönsted-type acid sites.³¹

Our results therefore indicate that although chlorination of the activated carbons increases their total surface acidity (as determined by measurement of the pH_{PZC}), it also decreases their Brönsted acidity (as determined by the dehydration of 2-propanol). These results can be explained by the effects introduced into the graphene layers by the chlorine covalently bound to their edges. Thus, chlorine introduces two opposing inductive and resonance effects in the aromatic rings,³¹ which are responsible for the withdrawal and release of electrons, respectively, from/to the graphene layers.

The inductive effect would strengthen very weak acidic oxide sites by withdrawing electrons from the graphene layers, thus increasing their Brönsted acidity.^{20,21} Conversely, the resonance effect would delocalize lone electron pairs from chlorine in the graphene layers, creating Lewis-type acid sites on chlorine. In addition, the delocalization of electrons in the graphene layers would weaken the acidic oxide sites. Thus, the inductive effect would increase Brönsted acidity, whereas the resonance effect would decrease Brönsted acidity but create new Lewis-type acid sites. The present results indicate that the resonance effect predominates over the inductive effect in these chlorinated activated carbons, and that the increase in Lewis acidity is greater than the decrease in Brönsted acidity. As a result, the total surface acidity of the chlorinated activated carbon increases with respect to the original carbon.²²

Surface Acidity of the Supported Catalysts. Results obtained in the decomposition reaction of 2-propanol are compiled in Tables 3 and 4 for catalysts from the We and Wa series, respectively. The catalysts from the We series were much more active than those from the Wa series, because of the higher dispersion of the former.¹⁹ In both series, the propene formation rate (r_p) was much higher than the acetone formation rate (r_A), demonstrating that all were essentially dehydration catalysts. As found in the supports, r_p decreased when the chlorine content

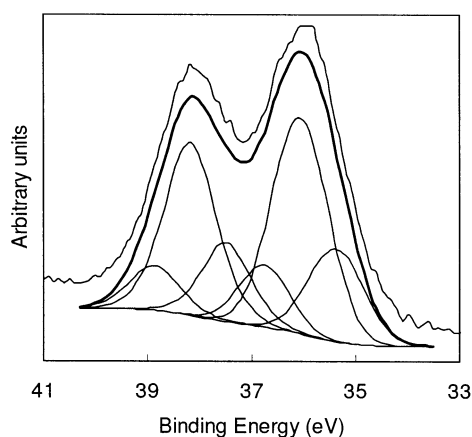


Figure 1. Curve-fitted W_{4f} core-level spectra for catalyst H1We pretreated in wet air at 623 K for 6 h and used in the decomposition reaction of 2-propanol.

TABLE 5: Quantitative Results from XPS of Catalysts Pretreated in Wet Air at 623 K for 6 h before and after Their Use (U) in the Decomposition Reaction of Isopropanol

catalyst	% (W ^{Cl}) _{XPS} ^a	% W _{XPS}	(W ⁵⁺ /W _T) _{at}	% W _{XPS} /% W _{TOTAL}
HWe		17.79	0.00	2.6
HWe (U)		16.98	0.00	2.5
H1We	5.15	22.51	0.00	3.0
H1We (U)	2.92	19.35	0.25	2.6
H2We	7.64	25.30	0.00	3.3
H2We (U)	6.60	20.68	0.07	2.7
HWa		15.10	0.00	2.0
HWa (U)		9.40	0.10	1.3
H1Wa	2.86	13.37	0.00	1.8
H1Wa (U)	1.71	8.96	0.00	1.2
H2Wa	3.16	10.61	0.00	1.3
H2Wa (U)	4.36	10.02	0.06	1.2

^a Tungsten atoms bound to chlorine.

of the support increased. This can be related to the formation of W–Cl bonds, which increased with the chlorine content of the support as previously reported.¹⁹

The pH_{PZC} values of the catalysts are shown in Tables 3 and 4 for both series of catalysts. The pH_{PZC} was similar in all Wa-series catalysts, probably due to their low dispersion. However, the pH_{PZC} of the We-series catalysts decreased when the chlorine content of the support increased, as previously found for the supports. Therefore, the chlorine of the support increases the total surface acidity of tungsten oxide supported on activated carbon. However, and as found with the supports, this increase in acidity is due to an increase in Lewis-type acid centers, because the Brönsted acidity is decreased, as shown by the decrease in r_p values.

After the catalysts were used in the decomposition reaction of 2-propanol, they were again characterized by XPS. Figure 1 depicts the XP spectrum for the W_{4f} levels of the used catalyst H1We (U), as an example, and the atomic and mass ratios obtained from the spectra are compiled in Table 5. The $W_{4f_{7/2}}$ core-level spectra of most of the used catalysts supported on chlorinated activated carbons showed three components: at around 35.2, 36.0, and 36.6 eV. The first peak was assigned to W(V), the second one to W(VI) in W–O bonds, and the third to W(VI) in W–Cl bonds. The peak assigned to W(V) appeared at 0.7 eV lower than that corresponding to W(VI)³² and was clearly distinguishable in the spectra. In the O_{1s} level spectra, it was not possible to distinguish the W(V)–O component because the BE of this oxygen was very little shifted from the BE of oxygen bound to W(VI). In fact, there is a BE shift of only 0.2–0.5 eV from WO_3 to WO_2 .^{33,34}

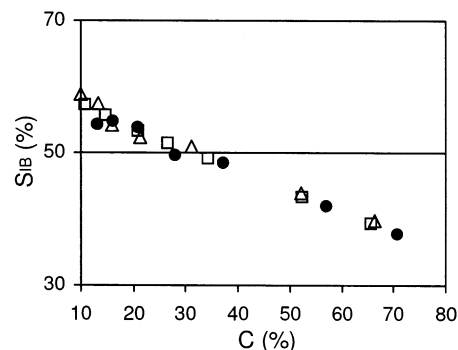
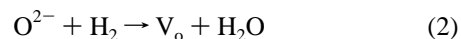


Figure 2. Variation in the selectivity to isobutene against total conversion for catalysts from series We: HWe (●); H1We (□); H2We (Δ).

Formation of W(V) occurred during the reaction, because the catalysts contained only W(VI) after the pretreatment in wet air at 623 K, as previously demonstrated.¹⁹ Therefore, tungsten trioxide particles are partially reduced by some of the products or the reactant during the reaction. Thus, H_2 was produced during the reaction as a consequence of the formation of acetone, and although its formation was very low, the decomposition of 2-propanol was followed for several hours. Dihydrogen can produce a surface deoxygenation of the tungsten oxide particles according to



where V_o is an oxygen vacancy, so that two W(VI) ions would be reduced to W(V) to maintain electrical neutrality. The appearance of these vacancies can mean that octahedral WO_6 units in the WO_3 structure pass from corner- to edge-sharing, bringing about a restructuring of the tungsten oxide particles. This can give rise to variations in the % W_{XPS} /% W_{TOTAL} ratio after the decomposition reaction of the 2-propanol. Thus, Table 5 shows a decrease in the above ratio after the reaction, due to an increase in the tungsten oxide particle size.

In general, the number of W–Cl bonds decreased during the reaction, due to their hydrolysis by the water produced in the formation of propene.

Skeletal Isomerization of 1-Butene. The skeletal isomerization of 1-butene is catalyzed by acid sites of Brönsted type,³⁵ whereas Lewis surface acid sites seem to be less important in this reaction.^{36,37} The production of isobutene from this reaction is selectively achieved by a monomolecular mechanism,^{35–39} and the byproducts (e.g., C_3 – C_5 or C_2 – C_6) are produced by a bimolecular mechanism that involves dimerization of butenes and isobutene, followed by breakdown of the octenes formed.

In all cases, the product distribution obtained after pretreatment in wet air of the supported catalysts showed that isobutene (IB) and *trans*-2-butene (T2B) were the main reaction products. Neither C_3 – C_5 nor C_2 – C_6 byproducts were obtained. Therefore, the reaction on these catalysts follows a monomolecular mechanism that produces both skeletal and double bond isomerization. This behavior was previously reported in other tungsten catalysts supported on activated carbon.¹⁷

Selectivity in the production of isobutene, S_{IB} , against conversion is depicted in Figures 2 and 3 for catalysts of the We and Wa series, respectively. In all cases, S_{IB} linearly decreased with increased conversion, reaching a value of 50% for a total conversion of 30%.

Activity results obtained with catalysts of the We series at 331 K and of the Wa series at 338 K are compiled in Tables 6 and 7, respectively. The We series of catalysts were more active

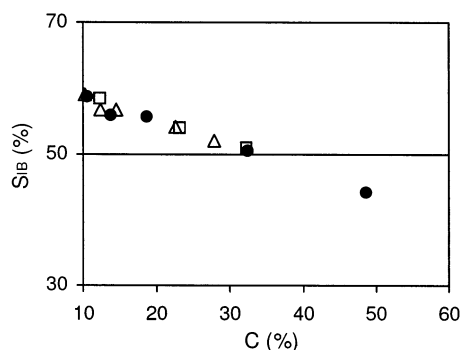


Figure 3. Variation in the selectivity to isobutene against total conversion for catalysts from series Wa: HWa (●); H1Wa (□); H2Wa (Δ).

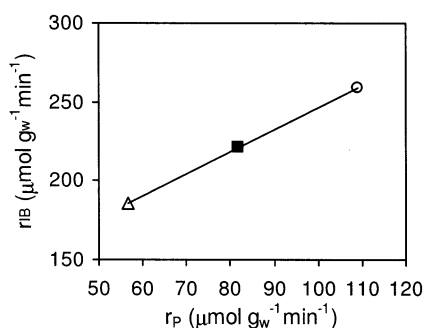


Figure 4. Variation in the activity to obtain isobutene at 331 K against the activity to obtain propene at 363 K for catalysts from series We: HWe (○); H1We (■); H2We (Δ).

TABLE 6: Results Obtained in the Skeletal Isomerization of 1-Butene at 331 K on Catalysts from Series We after Their Pretreatment in Wet Air at 623 K for 6 h

catalyst	C (%)	r_{IB} ($\mu\text{mol g}_w^{-1} \text{min}^{-1}$)	S_{IB} (%)
HWe	8.5	258.9	54.1
H1We	7.5	221.6	57.2
H2We	6.2	185.4	58.8

TABLE 7: Results Obtained in the Skeletal Isomerization of 1-Butene at 338 K on Catalysts from Series Wa after Their Pretreatment in Wet Air at 623 K for 6 h

catalyst	C (%)	r_{IB} ($\mu\text{mol g}_w^{-1} \text{min}^{-1}$)	S_{IB} (%)
HWa	8.2	262.1	60.1
H1Wa	6.0	176.9	55.5
H2Wa	5.6	158.4	59.3

than the Wa series because of the better dispersion of the former, and r_{IB} values decreased with increases in the chlorine content of the support. These results are similar to those found in the dehydration of 2-propanol, because both reactions need surface acid sites of Brönsted type. Thus, Figure 4 shows that there is a linear relationship between r_{IB} and r_P for catalysts from the We series. Therefore, although the presence of chlorine on the support increased its total surface acidity, it did not favor the skeletal isomerization of 1-butene.

Conclusions

When chlorine is fixed to activated carbons it introduces two opposing effects on the graphene layers, inductive and resonance effects that are responsible for the respective withdrawal and release of electrons from the layers. The inductive effect increases Brönsted acidity, whereas the resonance effect decreases this acidity but increases Lewis-type surface acidity, so that the net effect is an increase in total surface acidity. In

tungsten oxide supported on activated carbons, the chlorine content of the support has a similar effect on the surface acidity of the catalysts. The catalysts used in the decomposition reaction of 2-propanol, in the present study, are essentially of dehydration type, and their activity decreases when the chlorine content of the support increases. During this reaction, tungsten oxide is partially reduced to W(V) in most of the catalysts. This reduction is produced by the hydrogen formed as a consequence of the production of acetone. This creates oxygen vacancies that in turn produce a restructuring of the metal oxide particles, giving rise to a decrease in the % W_{XPS}/W_{total} ratio of the supported catalysts.

In the isomerization reaction of 1-butene, all catalysts produced only isobutene and *trans*-2-butene. The selectivity to produce isobutene decreases when the reaction temperature or total conversion increases. As in the dehydration of 2-propanol, the activity to produce isobutene decreases when the chlorine content of the support increases, because both reactions depend on the amount and strength of surface sites of Brönsted type.

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