Surface-Treated Activated Carbons as Catalysts for the Dehydration and Dehydrogenation Reactions of Ethanol

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Two activated carbons were prepared from olive stones with different degrees of activation and oxidized with a $(NH_4)_2S_2O_8$ solution for variable periods of time to introduce different amounts of oxygen surface complexes. Samples so prepared were characterized to know their surface area, porosity, and surface chemistry and then were used as catalysts in the conversion reactions of ethanol. The dehydration reactions to obtain ethene and ether only occurred on the oxidized samples, where carboxyl groups placed on the external surface of the particles were responsible for these reactions. The dehydrogenation reaction to yield acetaldehyde took place on either acid or basic surface sites placed not only on the external surface, but also on some part of the internal surface. During the reaction some surface active sites for dehydrogenation were lost because some hydrogen remained bound to them. The presence of air in the reactant mixture cleaned some of these sites, increasing the dehydrogenation activity and decreasing the dehydration activity. Also studied was the effect on their activity of the pretreatments of the catalysts in He or H_2 flow at different temperatures up to 1273 K.

Introduction

The use of carbon materials as catalysts and as catalyst supports has been reviewed recently.[1] Applications of these solids in catalysis are due to the versatility of their surface properties, such as surface area, porosity, and surface chemistry. Of these three properties, the surface chemistry is probably the most important in the catalytic processes taking place on the surface of these solids.

Surface chemistry of carbon materials is basically determined by the acidic and basic character of the carbon surfaces. The acidic behavior generally is, associated with oxygen surface complexes or oxygen functionalities such as carboxyls, lactones, and phenols. Other oxygen functionalities such as pyrone-, chromene-, ether-, and carbonyl-type structures give basic properties to the carbon surface.[2−9] All these oxygen surface complexes can be introduced on carbons by treatments with different oxidants either in liquid or gas phase. However, although some functionalities are able to act as basic sites, the basic properties of the carbon surfaces are not yet well understood, because some authors[3,10−13] have identified Lewis basic sites located at the π-electron−rich regions within the basal planes of graphitic microcrystals, away from the edges. Thus, the number of these basic sites would decrease with the fixation of oxygen surface complexes, essentially on the edges of the microcrystals, because these would decrease the delocalized π-electrons. Support for the existence of these Lewis basic sites comes from results that show a decrease in acid adsorption for a small increase in the oxygen content of the carbons[3] and more recently from measurements of heats of neutralization.[14,15]

Dehydration and dehydrogenation of alcohols are among the reactions most commonly used to test for acid−base catalysts, and these reactions have been studied extensively in inorganic oxides.[16−23] The dehydrogenation products, aldehyde or ketones, are preferentially formed on basic sites, whereas the dehydration products, olefins and ethers, are favored on acid sites. However, these reactions catalyzed by carbon materials have not been studied as extensively as with other materials. Thus, Szymanski et al.[24−26] studied the conversion reactions of different alcohols and suggested that the dehydrogenation reaction takes place simultaneously on Lewis basic and acid sites located at the external surface of the particles. The dehydration reaction takes place, according to the same authors, on acid sites essentially located at the external surface of the particles.

Grunewald and Drago[27] also studied the conversion reactions of ethanol catalyzed by carbon. When ethanol, diluted in N_2, passed over the catalyst at 503 K, the main product obtained was ethene, but the activity of the catalyst fell to zero in a few hours. However, if the carrier gas was switched to air, the catalyst regained activity immediately, and in these conditions acetaldehyde and ethyl acetate were the major products. These authors indicated that the surface active sites were reduced by ethanol and regenerated by air. The mechanism invoked was acid catalysis. Thus, a Lewis site subtracted a hydride and a Brönsted site protonated the alcohol. The subsequent loss of a proton from the former species yielded an aldehyde and loss of water, and a proton from the latter species yielded ethene.

Therefore, it seems that certain contradictions exist between the mechanism suggested by Szymanski et al.[24−26] for the dehydrogenation reaction and that of Grunewald and Drago.[27] Thus, for Szymanski et al. the reaction involved the simultaneous action of basic and acid Lewis sites, whereas for Grunewald and Drago it involved Lewis acid sites, which were completely deactivated with the reaction time when the carrier gas was inert.

Therefore, the aim of the present work was to gain more insight into the conversion reactions of ethanol on activated carbons with different surface properties. For this purpose, two activated carbons with different surface area and porosity were chosen. These were oxidized with $(NH_4)_2S_2O_8$ solutions for

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different periods of time to introduce variable amounts of oxygen surface complexes. It has been shown elsewhere,[28,29] that this oxidant treatment introduces strong acid groups and does not significantly modify the surface area and porosity of the original carbon. Thus, the relationship between the oxygen surface complexes and the activity and selectivity of the catalysts was studied.

Experimental Section

The preparation and characteristics of the activated carbons used in this work were reported elsewhere.[29] The raw material, olive stones, was carbonized in N_2 flow at 1273 K and steam activated at 1103 K to yield two activated carbons with 20% and 46% burnoff, which will be referred to in the text as AZ20 and AZ46, respectively. These activated carbons were oxidized with a saturated solution of $(NH_4)_2S_2O_8$ at 298 K for different periods of time up to a maximum of 24 h.[29] All oxidized samples were washed with distilled water until there was an absence of sulfates in the washing water. The oxidation time is added to the name of the activated carbon, thus, AZ20-2 means activated carbon AZ20 oxidized for 2 h. The original and oxidized activated carbons were characterized by N_2 and CO_2 adsorption at 77 and 273 K, respectively. Mercury porosimetry up to 2600 $kg \cdot cm^{-2}$ and He and Hg densities were determined. The surface chemistry of the samples was studied by temperature-programmed desorption followed by mass spectrometry (TPD-MS), Fourier transform infrared, titrations with bases and HCl, and measurements of the pH of the point of zero charge. All the results obtained with these techniques have been widely discussed elsewhere.[29]

The decomposition reactions of ethanol were conducted in a plug-flow microreactor working at atmospheric pressure and using He or air as the carrier gas. The concentration of ethanol in the reactant mixture was generally 0.32 vol %. Other ethanol concentrations were also used. For this purpose, the carrier gas was saturated with ethanol that was kept in a cold trap at different temperatures.

The amount of catalyst used was approximately 0.5 g, which was heat treated in He flow at 453 K for 2 h before studying its activity. The effect of other heat treatments up to 1273 K in He or H_2 flow on the activity of the catalysts was also studied. After the heat treatments the samples were cooled to the reaction temperature (which ranged from 413 to 453 K) and the He or H_2 flow changed to the reactant mixture, 60 $cm^3 \cdot min^{-1}$. This mixture was allowed to flow through the catalyst for 30 min before the analysis of the reaction products. After this, only the carrier gas (He or air) flowed through the catalyst for 30 min, and at the same time a new reaction temperature was stabilized; then the reactant mixture was again introduced into the reactor to study the reaction at different temperatures.[30] In all cases the space velocity was 20 h^{-1}, which was calculated from the ethanol flow through the catalyst and its particle density from mercury porosimetry.[29]

Analysis of the reaction products was done by on-line gas chromatography using a Perkin-Elmer gas chromatograph, model 8500, with flame ionization detection and a column Carbopack B80/120. The flame detector was previously calibrated by injecting known amounts of the reaction products. The activity to obtain acetaldehyde, ethene, and ether was estimated from eq 1

$$r_x = \frac{F_{\mathrm{EtOH}} \cdot C_x}{W} \tag{1}$$

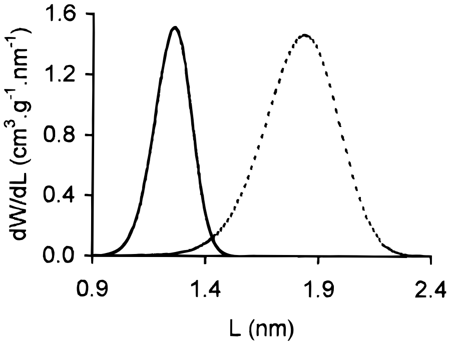


Figure 1. Micropore size distribution for activated carbons AZ20 (—) and AZ46 (- - -).

where r_x is the activity to obtain the species x; F_{EtOH} is the ethanol flow through the catalyst in moles per s, C_x is the ethanol conversion to the species x, and W is the weight of the sample in grams.

Results and Discussion

Characteristics of the Catalysts. The micropore size distributions (MSD) for samples AZ20 and AZ46 are depicted in Figure 1. These MSD were obtained from the CO_2 adsorption data by applying the equation deduced by Dubinin and Stoeckli.[31] The MSD of this Figure indicates that the most activated sample, AZ46, has a wider microporosity and greater micropore volume than sample AZ20.

Other surface characteristics of the original and oxidized activated carbons from the series AZ20 and AZ46 are compiled in Table 1. The oxidation of AZ20 for different periods of time up to a maximum of 24 h did not affect either the surface area or the pore texture of the samples, although the oxygen content of the original sample increased from 1.20% to 6.64% after 24 h of oxidation.

For the same time of oxidizing treatment the samples of series AZ46 were able to fix a larger amount of oxygen than samples from series AZ20, increasing from 1.30% to 11.20% after 24 h treatment. This was due to a greater surface area and more developed meso- and macroporosity and a wider and greater microporosity of the samples from series AZ46 than from series AZ20.

The oxidation of AZ46 now produces a very slight decrease in the surface area and porosity of the samples, probably because the original carbon has a higher degree of activation than AZ20, and, therefore, the pore walls are thinner and destroyed more easily, as reported previously for other oxidizing treatments.[28]

Some of the parameters that characterize the surface chemistry of the catalysts are also compiled in Table 1. Thus, the total surface acidity, as measured by NaOH titration, increases with oxidation time for both series of activated carbons because of the fixation of carboxyl, lactonic, and phenolic groups as shown elsewhere.[26] For the same oxidation time, samples from the series AZ46 have a greater total acidity than samples from the series AZ20 because of their higher oxygen content. As a result of the increase in surface acidity of the activated carbons with oxidation time there is a marked decrease of their pH_{PZC}. Thus, the original activated carbons have a basic pH_{PZC}, around 11, which sharply decreases during the first 30 min of treatment, and more gradually thereafter. The total surface basicity, as titrated with HCl, is also given in Table 1, and it decreases when the degree of oxidation or total surface acidity increases, indicating that basic surface sites are essentially associated with the absence of oxygen-containing groups which are predominantly of acidic nature.

TABLE 1: Surface Characteristics of Activated Carbons

sample	O, %	S_{N_2}, $m^2 \cdot g^{-1}$	W_0[a], $cm^3 \cdot g^{-1}$	V_{meso}, $cm^3 \cdot g^{-1}$	V_{macro}, $cm^3 \cdot g^{-1}$	NaOH, $meq.g^{-1}$	HCl, $meq \cdot g^{-1}$	pH_{PZC}
AZ20	1.19	631	0.310	0.238	0.099	0.21	0.76	10.99
AZ20-0.5	2.48	608	0.314	0.231	0.089	0.41	0.37	3.26
AZ20-10	5.89	625	0.313	0.230	0.080	0.96	0.20	2.38
AZ20-24	6.64	637	0.304	0.206	0.080	1.09	0.18	2.31
AZ46	1.30	914	0.514	0.251	0.130	0.57	0.70	10.85
AZ46-0.5	5.57	902	0.510	0.252	0.129	0.93	0.25	3.04
AZ46-10	10.50	815	0.442	0.254	0.125	2.40	0.14	2.30
AZ46-24	11.20	810	0.436	0.240	0.120	2.72	0.21	2.20

[a] W_0 = volume of micropores obtained from DA equation applied to CO_2 adsorption at 273 K.

TABLE 2: Total Conversion and Product Distribution (%) at 453 K from a He/Ethanol Mixture

sample	conversion	Acet[a]	Ethene	Ether	1,3-But[b]	EtAc[c]
AZ20	1.0	100.0				
AZ20-0.5	17.3	10.6	25.6	62.2	0.2	1.4
AZ20-10	21.0	11.5	25.2	60.3	0.4	2.6
AZ20-24	22.6	10.8	26.3	59.5	0.3	3.1
AZ46	1.5	100.0				
AZ46-0.5	8.9	25.6	17.3	53.4	0.4	3.3
AZ46-10	14.0	22.0	17.0	52.3	0.9	7.9
AZ46-24	16.0	19.8	16.2	55.6	0.5	7.9

[a] Acetaldehyde. [b] 1,3-Butadiene. [c] Ethyl acetate.

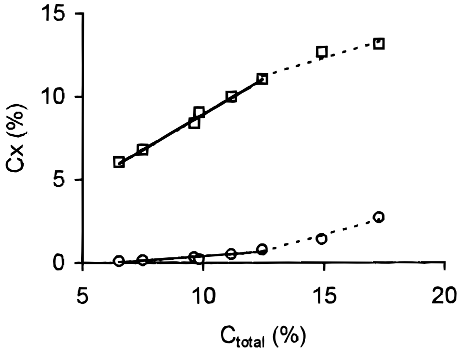
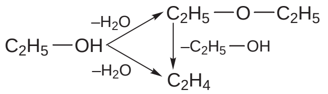


Figure 2. Optimum performance envelope (OPE) curves for ethanol conversion on catalyst AZ20-0.5. Fractional conversion to a particular reaction product (C_x) versus total conversion (C_{Total}). □, ether; ○, ethene.

Product Distribution and Activity of the Catalysts. Total conversion and product distribution obtained with a He/ethanol mixture at a reaction temperature of 453 K, with some selected catalysts from the series AZ20 and AZ46, previously heat treated at 453 K in He flow for 2 h, are shown in Table 2. The original carbons AZ20 and AZ46 are dehydrogenation catalysts producing acetaldehyde as the only reaction product. The oxidized carbons are able to give both dehydrogenation and dehydration reactions. The major product obtained is ether. The conversion increased with the oxidation time, especially at the beginning of oxidation, due to the formation of the dehydration products. Samples from series AZ20 have higher conversion than samples from series AZ46, although the former have a lower oxygen content than the latter. This behavior will be explained later.

Acetaldehyde, ether, and ethene were obtained directly from ethanol by dehydrogenation and dehydration; i.e., they are primary reaction products coming from ethanol through a parallel reaction network. A primary product is defined as that which is produced from the reactant no matter how many surface intermediates are involved in its formation. However, ether can be an unstable product under the reaction conditions. Thus, Szymanski and Rychlicki[25] found that dipropyl ether obtained by the catalyzed dehydration of propanol with a carbon catalyst was decomposed during the reaction giving propene and 2-propanol. Campelo et al.[23] also found, with an $AlPO_4$ catalyst, that ether was unstable and decomposed in the corresponding alcohol and olefin. For this reason, we have developed the corresponding optimum performance envelope (OPE) curves by plotting the fractional conversion to ether and ethene against the total conversion for different weight ratios of the catalyst to the alcohol introduced as described by Ko and Wojciechowski.[32] The OPE curves obtained in the case of the catalyst AZ20-0.5 are plotted in Figure 2, as an example. Above a total conversion of 12%, a downward deviation occurs in the ether conversion, which corresponds with an upward deviation in ethene formation. This is because ether also participates in the formation of ethene. Thus, ethene is a primary product plus a secondary stable reaction product. The formation pathway of ether and ethene from ethanol dehydration on these carbon catalysts is given in eq 2.



$$C_2H_5{-}OH \begin{cases} \xrightarrow{-H_2O} C_2H_5{-}O{-}C_2H_5 \\ \xrightarrow{-H_2O} C_2H_4 \end{cases} \qquad C_2H_5{-}O{-}C_2H_5 \xrightarrow{-C_2H_5-OH} C_2H_4 \tag{2}$$

Moreover, the decomposition reaction of ether from a He/ether mixture at 453 K was also studied with the catalysts AZ20 and AZ20-20. In the sample AZ20 there was no reaction, whereas carbon AZ20-20 was able to decompose the ether giving a mixture of acetaldehyde, ethene, and ethanol. In this case, part of the ethanol formed underwent the dehydrogenation reaction to acetaldehyde. Thus, the decomposition of ether only took place on the oxidized samples, where its formation by dehydration of ethanol was possible.

Table 2 also shows that 1,3-butadiene and ethyl acetate were obtained as secondary products; 1,3-butadiene was obtained by the Prin's reaction,[33] in which acetaldehyde reacted with ethene to yield an enol that produced 1,3-butadiene by dehydration.

Ethyl acetate is formed by a dehydrogenation reaction between the acetaldehyde formed initially and ethanol molecules or surface ethoxy groups. The catalysts containing transition metal elements, active for dehydrogenation of ethanol, produce large amounts of ethyl acetate, essentially in the high conversion range.[34] In these catalysts the surface active sites for ethyl acetate formation are presumed to be the same as for the dehydrogenation of ethanol, therefore, it is difficult to inhibit the formation of this compound on the above-mentioned catalysts. This mechanism also has been suggested for the reaction of an air/ethanol mixture on a Ni catalyst supported on an activated carbon.[26]

Results given in Table 2 indicate that ethyl acetate was produced only on the oxidized catalysts, and its percentage increased with the increase in total surface acidity. Nevertheless, ethyl acetate was not produced on the original carbons AZ20 and AZ46, whose surfaces have a marked basic character with a pH_{PZC} of about 11. This means that not all the surface active

TABLE 3: Activity of the Catalysts for Acetaldehyde, Ethene, and Ether Formation at 453 K from a He/Ethanol Mixture[a]

sample	r_{acet}, μmol·g^{-1}·s^{-1} × 10^2	r_{ethene}, μmol·g^{-1}·s^{-1} × 10^2	r_{ether}, μmol·g^{-1}·s^{-1} × 10^2	E_{acet}, kJ·mol^{-1}	E_{ethene}, kJ·mol^{-1}	E_{ether}, kJ·mol^{-1}
AZ20	0.28			58.7 ± 0.9		
AZ20-0.5	0.33	0.81	3.92	48.1 ± 0.6	175.5 ± 5.3	65.7 ± 2.6
AZ20-10	0.43	0.94	4.48	51.9 ± 1.1	153.7 ± 1.6	60.0 ± 1.8
AZ20-24	0.41	1.00	4.55	49.4 ± 2.6	149.7 ± 1.7	58.2 ± 3.2
AZ46	0.43			60.3 ± 1.3		
AZ46-0.5	0.43	0.29	1.81	67.5 ± 4.2	152.7 ± 1.0	74.0 ± 3.3
AZ46-10	0.55	0.43	2.62	63.3 ± 4.2	143.8 ± 3.5	69.0 ± 3.7
AZ46-24	0.53	0.44	2.99	59.4 ± 1.4	138.0 ± 5.2	59.6 ± 4.4

[a] Activation energies in the temperature range, 413−453 K.

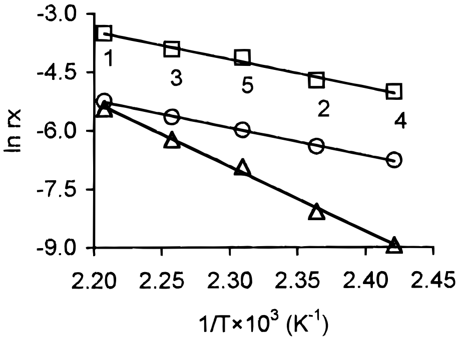


Figure 3. Arrhenius plots for acetaldehyde, ethene, and ether formation on catalyst AZ46-24. □, ether; △, ethene; ○, acetaldehyde.

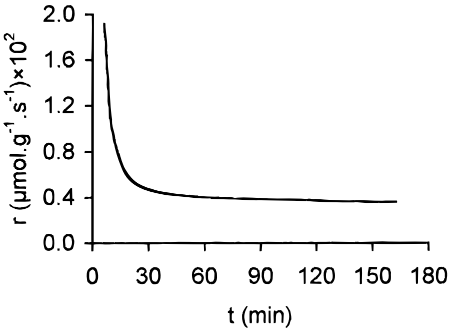


Figure 4. H_2 evolution at 453 K against reaction time for catalyst AZ20-20.

centers of the carbon involved in the dehydrogenation of ethanol are capable of producing ethyl acetate.

The activity values for acetaldehyde, ethene, and ether formation, r_{acet}, r_{ethene}, and r_{ether}, respectively, at a reaction temperature of 453 K on some selected catalysts from both series of activated carbons are given in Table 3, together with the activation energy to obtain the products above within the temperature range between 413 and 453 K. These activation energies were obtained from Arrhenius plots similar to that shown in Figure 3, as an example. The numbers for the experimental points indicate the order in which they were determined and there is as good agreement for data obtained when either increasing or decreasing temperatures cycles. This is a good indication that, in the experimental procedure followed and explained above, the surface active sites remained clean in each activity measurement and the catalyst did not deactivate. This behavior is different from that found previously by Grunewald and Drago.[27]

If there were no deactivation for acetaldehyde formation, it would be possible to detect H_2 evolution from the catalyst during the reaction time. Thus, the hydrogen produced during the conversion reaction of ethanol was followed with a mass spectrometer as a function of reaction time. The results obtained with catalyst AZ20-20 are depicted in Figure 4, as an example, which indicates that there is a large decrease in H_2 evolution at the beginning of the reaction time reaching a steady-state evolution at approximately 30 min of reaction. These results show that most of the active sites for the dehydrogenation reaction are lost at the beginning of the reaction by hydrogen chemisorption. However, some of these were not deactivated, and these were responsible for the activity measured on these catalysts.

The dehydration of ethanol (Table 3) only takes place with oxidized samples, increasing the activity with the increase in total surface acidity for both series of samples. This indicates that the dehydration reactions only occur on acid surface sites of the Brönsted type. In this process, the formation of ether is more favored than that of ethene as shown by the lowest values of E_{ether} compared with E_{ethene}. Similar behavior was found in the dehydrogenation of ethanol on different $AlPO_4$ catalysts.[23] These values decreased slightly when the number of acid surface sites of the Brönsted type increased with oxidation.

The dehydration activities (Table 3), r_{ethene} and r_{ether}, are higher in oxidized samples from series AZ20, despite their lower oxygen content and total surface acidity than samples from series AZ46 (compared at the same oxidation time). This behavior could be explained if the dehydration reactions took place only on the external surface of the particles. Thus, as shown elsewhere,[29] due to the larger molecular size of the CO_2-evolving groups, such as the carboxyl and lactone groups, there will be some hindrance to their formation in the narrower pores of sample AZ20 and, therefore, they will be fixed on the sample more slowly than in sample AZ46, which has a more developed and wider porosity. Therefore, the relative amount of voluminous acid groups on the external surface of samples from series AZ20 (especially at the beginning of the oxidation treatment) would be higher than in the samples from the series AZ46. This explains the much higher values of r_{ethene} and r_{ether} in sample AZ20-0.5 than in sample AZ46-0.5, because in the latter sample, and in accordance with the arguments above, most of the acidic groups would be on the internal surface of the particles inaccessible for dehydration. Likewise, the increase in oxidation time between 0.5 and 24 h augments the r_{ethene} and r_{ether} values for samples from series AZ46 to a greater extent (52% and 65%, respectively) than for samples from AZ20 (23% and 16%, respectively), because as oxidation time increases, the samples from series AZ46 increase the carboxyl acid groups placed on the external surface to a greater extent than the samples from series AZ20.

The original carbons from both series, AZ20 and AZ46, had a basic character (Table 1) and were only dehydrogenation catalysts (Table 3). When these samples were oxidized the total surface acidity, as titrated with NaOH, increased and the total surface basicity, as titrated with HCl, decreased (Table 1). However, for both series of samples r_{acet} values increased with oxidation time as shown in Table 3. This trend could be

TABLE 4: Activity of the Catalysts for Acetaldehyde, Ethene, and Ether Formation at 453 K from Both He/Ethanol and Air/Ethanol Mixture

sample	mixture	r_{acet}, $\mu mol \cdot g^{-1} \cdot s^{-1} \times 10^2$	r_{ethene}, $\mu mol \cdot g^{-1} \cdot s^{-1} \times 10^2$	r_{ether}, $\mu mol \cdot g^{-1} \cdot s^{-1} \times 10^2$
AZ20	He/ethanol	0.28		
AZ20-2		0.42	0.91	4.28
AZ20-6		0.43	1.06	4.42
AZ20-15		0.41	0.96	4.46
AZ20	air/ethanol	0.66		
AZ20-2		0.63	0.33	1.55
AZ20-6		0.70	0.50	2.00
AZ20-15		0.74	0.67	3.24

explained if the dehydrogenation reaction were also catalyzed by Lewis acid surface sites which would act by subtracting a hydride. Thus, the dehydrogenation reaction seems to occur either on basic or acid surface sites, but not necessarily at the same time on both sites.

On the other hand, with other solid catalysts the dehydrogenation reaction did not proceed on acid−base sites. Thus, it was reported[35,36] that on highly dehydrated silica the reaction took place on silanol surface groups on which dissociative adsorption of ethanol occurs. In the oxidized carbons, the ether groups that are present on these samples[29] might act in a similar way, and alternatively, dehydrogenation could also proceed as eq 3.

$$\mathrm{C{-}O{-}C + CH_3{-}CH_2OH \rightleftharpoons C{-}OH + C{-}OC_2H_5 \rightarrow C{-}O{-}C + CH_3{-}COH + H_2} \quad (3)$$

Samples from series AZ46 have slightly higher r_{acet} values than samples from series AZ-20, which indicates that in the dehydrogenation reaction not only the external surface groups were available for catalyzing this reaction but also some of the internal surface groups.

The conversion reactions of ethanol at 453 K were also studied with an air/ethanol mixture with selected catalysts from both series of samples. The activity values for samples from series AZ20 are compiled in Table 4 together with those obtained with a He/ethanol mixture at 453 K for comparison. These data show that when the carrier gas was air instead of He there was a marked increase in the activity for acetaldehyde formation and a decrease in both r_{ethene} and r_{ether}. Similar results were obtained with samples from series AZ46. Thus, the presence of air in the reactant mixture favors the removal of hydrogen (coming from the acetaldehyde formation) that remained chemisorbed on the surface active sites at the first stage of the reaction (see Figure 4) producing water, which, in turn, partially inhibited the dehydration reactions.

Effect of the Pretreatments of the Catalysts on Their Product Distribution and Activity. Sample AZ46-20 was chosen to carry out these experiments. Different portions of this sample were pretreated, in the same reactor, under He or H_2 flow at different temperatures up to 1273 K, with a soak time of 2 h, before carrying out the conversion reactions at 453 K in a He/ethanol mixture. The samples were not exposed to the atmosphere either after the pretreatment or before the reaction.

The heat treatment of carbon materials in H_2 instead of in an inert gas, like He, favors the elimination of the oxygen surface complexes, stabilizes some of the reactive sites of the carbon surface through the formation of stable C−H bonds, and gasifies the unsaturated carbon atoms that are more reactive.[13] All these effects can affect the surface active sites that are involved in the dehydrogenation and dehydration reactions of ethanol.

TABLE 5: Amounts of H_2, CO, and CO_2 Evolved from the Pretreated AZ46-20 Samples after Heating at 1273 K in He

pretreatment				
T (K)	atmosphere	H_2, $mmol \cdot g^{-1}$	CO, $mmol \cdot g^{-1}$	CO_2, $mmol \cdot g^{-1}$
453	He	0.03	3.85	1.53
653	He	0.10	3.45	0.56
873	He	0.06	2.05	0.16
1273	He	0.05	0.05	0.04
653	H_2	0.20	3.44	0.60
873	H_2	1.61	0.22	0.06
1273	H_2	0.37	0.05	0.00

TABLE 6: Total Conversion, *C*, and Activity of the AZ46-20 Catalyst for Acetaldehyde, Ethene, and Ether Formation at 453 K after Different Pretreatments from a He/Ethanol Mixture

pretreatment					
T (K)	atmosphere	C, %	r_{acet}, $\mu mol \cdot g^{-1} \cdot s^{-1} \times 10^2$	r_{ethene}, $\mu mol \cdot g^{-1} \cdot s^{-1} \times 10^2$	r_{ether}, $\mu mol \cdot g^{-1} \cdot s^{-1} \times 10^2$
453	He	15.4	0.56	0.45	2.99
653	He	1.5	0.20		
873	He	2.7	0.52		
1273	He	3.5	0.53		
453	H_2	12.5	0.49	0.38	2.24
653	H_2	1.3	0.29		
873	H_2	0.7	0.13		
1273	H_2	0.9	0.27		

The amounts of H_2, CO, and CO_2 desorbed from the pretreated samples, obtained from TPD experiments, are recorded in Table 5. Results obtained indicate that samples pretreated in H_2 have a higher H_2 content, which depends on the treatment temperature. Thus, pretreatment at 873 K leaves the greatest amount of hydrogen chemisorbed, because the oxygen surface complexes that remained after the pretreatment in He are reduced during the pretreatment in H_2, at the same time leaving a large amount of hydrogen bound to the nascent carbon atoms left behind.

Conversion and activity of the pretreated catalysts to produce acetaldehyde, ethene, and ether at 453 K are compiled in Table 6. Furthermore, all the pretreated catalysts at a temperature equal to or greater than 653 K also gave acetal (1,1′-dietoxyethane) and the pretreated samples at 1273 K gave butanol among the reaction products, which comes from secondary reactions of acetaldehyde.

Activity for acetaldehyde formation, r_{acet}, largely decreased when the pretreatment was carried out at 653 K in He but increased for higher pretreatment temperatures, indicating that the carbon sites left behind by the removal of oxygen complexes above 653 K were able to catalyze the dehydrogenation reaction. On the contrary, pretreated samples in H_2 above 653 K had a lower r_{acet}, because hydrogen was bound, during the pretreatment, to some of the surface carbon atoms left after reduction of the oxygen surface groups, making them inactive for dehydrogenation reaction. Sample pretreated at 873 K had the lowest activity because the largest amount of hydrogen was bound at that temperature. The catalyst pretreated either in H_2 or He at a temperature equal to or greater than 653 K had no activity for dehydration, indicating that the carboxyl acid groups are the only active sites for this reaction, because these groups are not stable at a temperature greater than 653 K.[37]

Conclusions

Acetaldehyde, ethene, and ether were the primary products obtained from the dehydrogenation and dehydration reactions.

Ethene was also a secondary product obtained from the decomposition of ether.

The dehydration reaction took place only on the oxidized samples. The activity to obtain dehydration products increased with the total surface acidity, these reactions were catalyzed by the carboxyl acid groups placed on the external surface of the particles.

The original activated carbons, which were basic catalysts, were only dehydrogenation catalysts producing acetaldehyde as the only reaction product. Formation of this compound increased with the oxidation of carbons. Thus, the dehydrogenation reaction seems to take place on either basic or acid surface groups. Furthermore, in the oxidized samples the presence of some oxygen surface complexes, such as ether groups, might also catalyze the dehydrogenation reaction as in the case of silanol groups in silica samples. Active sites placed on the external surface and also some of them placed on the internal surface of the samples participated in the dehydrogenation reaction.

At the beginning of the reaction some of the active sites for the dehydrogenation of ethanol were lost because hydrogen remained bound to them. However, the presence of air in the reactant mixture increased the dehydrogenation activity and decreased the dehydration activities, because the presence of air kept clean of hydrogen more active sites for dehydrogenation, producing water which inhibited the dehydration.

Pretreatment of the catalysts in H_2 at temperatures higher than 653 K decreases the activity for dehydrogenation caused by the bonding of H atoms with some of the surface active sites created after reduction of the oxygen surface complexes.

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