

# SURFACE TREATED ACTIVATED CARBONS AS CATALYSTS IN THE DEHYDROGENATION AND DEHYDRATION REACTIONS OF ETHANOL

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## Introduction

Dehydrogenation and dehydration of alcohols can proceed on carbons as catalysts due to their acid-base surface characteristics [1,2].

The mechanism of the dehydrogenation and dehydration over inorganic oxides is acid catalysis via Lewis or Brønsted sites to generate a carbocation or a protonated alcohol [3]. For alcohols over a carbonaceous material it has been suggested [1] typical Lewis acid catalysis for the dehydrogenation reaction. However, other authors [4] have suggested that Lewis base and Lewis acid sites participate simultaneously in the dehydrogenation process of alcohols on carbon materials. In case of ethanol the dehydrogenation reaction leads to acetaldehyde which can give further secondary reactions.

The aim of this work was to study the dehydration and dehydrogenation reactions of ethanol over an activated carbon that was chemically and thermally treated to introduce different amounts of oxygen surface complexes and with different nature.

## Experimental

An activated carbon obtained from olive stones was used in this work. The raw material was carbonized at 1273 K in N<sub>2</sub> flow and steam activated at 1103 K to yield an activated carbon with 46 %BO, which will be referred to in the text as AZ46. This activated carbon was oxidized with a saturated solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> for different periods of time up to a maximum of 24 h. The oxidation procedure was described elsewhere [5]. The oxidation time is added to the name of the activated carbon, thus AZ46-2 means activated carbon AZ46 oxidized for two hours.

The original and oxidized activated carbons were characterized by N<sub>2</sub> and CO<sub>2</sub> adsorption at 77 and 273 K, respectively; mercury porosimetry and He and Hg

densities in order to determine the surface area and pore texture of the activated carbon used.

The surface chemistry of the samples was studied by different techniques such as: TPD, FTIR, titrations with bases of different strength and HCl acid, and pH<sub>PZC</sub> measurements.

The decomposition of ethanol was conducted in a plug-flow microreactor working at atmospheric pressure and using He as carrier gas. The concentration of ethanol in the ethanol/He mixture was 0.32% by volume. The sample, 0.5 g, was previously heat treated in He at 453 K for 2 h and the decomposition reaction of ethanol was studied between 413 and 453 K. The analysis of the reaction products was performed by on-line-gas-chromatography using a column Carboxpack B 80/120 and FID.

## Results and Discussion

Some surface characteristics of selected activated carbons used in this work are given in Table 1.

Table 1. Characteristics of some of the activated carbons.

Sample	SN <sub>2</sub> m <sup>2</sup> .g <sup>-1</sup>	V <sub>T</sub> cm <sup>3</sup> .g <sup>-1</sup>	O %	NaOH meq.g <sup>-1</sup>	HCl meq.g <sup>-1</sup>
AZ46	914	0.895	1.30	0.57	0.70
AZ46-2	882	0.837	6.69	1.60	0.33
AZ46-5	820	0.823	8.45	2.10	0.61
AZ46-10	815	0.821	10.50	2.40	0.69
AZ46-24	810	0.796	11.20	2.72	0.87

The increase in the oxygen content of the samples makes the nitrogen surface area, SN<sub>2</sub>, and the total pore volume, V<sub>T</sub>, to decrease slightly. The total acidity of the samples as titrated with NaOH increases with the oxidation time and the total basicity, as measured with HCl, decreases at the beginning of the oxidation process increasing after around 30 min (data not given in the Table), reaching a higher value than that of the original sample after 24 h oxidation time. The correlation of the

$pH_{PZC}$  and the amount of oxygen per unit surface area ( $SN_2$ ) is depicted in Figure 1.

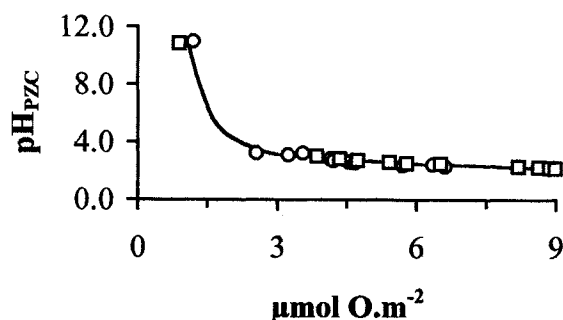


Figure 1. Relationship between the  $pH_{PZC}$  and oxygen content per unit surface area.

The products distribution obtained in the decomposition of ethanol at 453 K for the above activated carbons is shown in Table 2. The original activated carbon AZ46 only produces acetaldehyde (AcHO). However, all the oxidized samples give almost the same products distribution: acetaldehyde and the dehydration products ethylene, Et, and diethyl ether,  $Et_2O$ . Aside of this main products, other two products were formed as a result of secondary reactions. Thus, ethyl acetate, EtAc is the result of a secondary condensation reaction between acetaldehyde initially formed with another ethanol molecule or surface fragment. 1,3 butadiene, But, was also detected in a small proportion as a result of the Prins reaction between

and acetaldehyde molecule with another of ethene and further dehydration of the unsaturated alcohol formed.

Table 2. Product distribution (%) in the dehydration and dehydrogenation of ethanol at 453 K.

Sample	AcHO	Et	$Et_2O$	But	EtAc
AZ46	100	---	---	---	---
AZ46-2	23.8	18.5	50.9	0.8	5.9
AZ46-5	22.7	17.4	52.2	0.7	6.9
AZ46-10	22.0	17.0	52.3	0.9	7.9
AZ46-24	19.8	16.2	55.6	0.6	7.9

Table 3 shows the activity values for the main products formation at 453 K and the apparent activation energies in the temperature range of 413-453 K. The activity to obtain acetaldehyde  $r_{AcHO}$  increases from AZ46 to AZ46-2 and then remains constant with the oxidation time. This result indicate that both basic and acid surface sites are involved in the dehydrogenation reaction of ethanol.

The apparent activation energy for this reaction remains constant for all samples at a value around 60  $kJ.mol^{-1}$ . The activity to obtain ethylene and diethyl ether increases with the acidity of the activated carbon and the apparent activation energy to obtain this products by dehydration of ethanol decreases with the oxidation time of the original sample AZ46.

Table 3. Activity of the catalysts at 453 K and activation energy for the dehydration and dehydrogenation of ethanol.

Sample	C %	$r_{AcHO}$	$r_{Et}$ $\mu mol.g^{-1}.s^{-1} \times 10^2$	$r_{Et_2O}$	$E_{ac}$ $kJ.mol^{-1}$ (413-453 K)		
					$E_{acAcHO}$	$E_{acEt}$	$E_{acEt_2O}$
AZ46	1.5	0.43	---	---	60.3	---	---
AZ46-2	11.4	0.52	0.40	2.23	64.5	167.0	68.2
AZ46-5	13.4	0.55	0.42	2.52	63.4	155.5	70.0
AZ46-10	14.0	0.55	0.43	2.62	63.3	143.8	69.0
AZ46-24	16.0	0.53	0.44	2.99	59.4	138.0	59.6

### Acknowledgments

The authors wish to acknowledge the financial support of DGICYT, Project no. PB94-0754. A.M. acknowledges to the Universidad de Granada for the fellowship to carry out his third cycle studies.

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