

# MODIFICATION OF AN ACTIVATED CARBON BY THERMAL TREATMENT UNDER N<sub>2</sub>O, AIR AND HYDROGEN

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## Introduction

Activated carbon is a very versatile material and the knowledge and control of its surface chemistry allows to design truly unique catalysts for applications in different industrial reactions and processes [1, 2]. Previous results have shown that oxidized activated carbons were active for the oxidative dehydrogenation of ethylbenzene [3]. In this work, we report on the textural and chemical modifications induced by treating an activated carbon under nitrous oxide, air and hydrogen. These catalysts are to be tested in the oxidative dehydrogenation of isobutane.

## Experimental

An activated carbon Norit ROX 0.8 (CORIG) was used in the present study, which was subsequently exposed to thermal treatments in different atmospheres. Treatments using 20% nitrous oxide at 500°C (samples CN/180, CN/360, and CN/600), 5% oxygen at 425°C, (samples CO/360, CO/600) and 100% hydrogen at 950°C during 180 and 360 minutes (samples CH/180, CH/360) were carried out. The heating rate was 10°C/min starting from 25°C to the treatment temperature. The heating for the nitrous oxide and air oxidations was carried out under a nitrogen flow rate of 80 mL/min; when the final temperature was reached, 20 mL/min of nitrous oxide or 20 mL/min of air was then added during the treatment time. At the end of the heating treatment, the oxidant gas flow was stopped and the system left to cool freely to room temperature under a nitrogen flow of 80 mL/min.

The hydrogasification was carried out with a hydrogen flow of 150 mL/min, starting at 25°C to 950°C, and the temperature kept for 3 and 6 hours, then cooled down freely in hydrogen flow to ambient temperature and finally nitrogen was introduced to sweep the residual hydrogen. The burn off, as the ratio between the mass lost during the treatment and the initial dry mass, was determined for each sample. The activated carbon samples were characterized by elemental and proximate analysis, nitrogen adsorption at 77 K, thermogravimetry, Temperature Programmed Oxidation (TPO) and Temperature Programmed Desorption (TPD). The micropore and supermicropore

volumes were determined by the Dubinin method, while the mesoporous surface area was determined by the t method.

## Results and Discussion

Table 1 shows the results of the different treatments. For all treatments in nitrous oxide and oxygen an increase in volatile matter content was observed, which indicates an increase in surface functional groups, while for the samples treated in hydrogen this was not evident and on the contrary a strong decrease was observed. Also, a slight increase in nitrogen content was observed for the samples treated in nitrous oxide, with increasing residence times, which may imply nitrogen incorporation into the carbon matrix or in nitrogen surface groups.

The adsorption isotherms for all carbons used were of type I according to the IUPAC classification [4], and of class C as is described by Rodríguez Reinoso et al [5], since the large microporosity is accompanied by a well developed mesoporosity in such a way that the linear branch, at relatively high pressures, is not parallel to the pressure axis. The observed hysteresis is of the type H4, characterized by isotherm branches almost horizontal and parallel during an extensive range of the abscissa, which is associated with slit-shaped pores and type I isotherms.

The different treatments produce textural changes in the carbons. These changes are due to carbon gasification produced by oxidation, opening and enlarging existing pores, or creating new micropores. It can be observed that the nitrous oxide treatment generates a larger amount of micropores than the oxygen treatment which is more noticeable at larger burn offs. The carbon treated with hydrogen shows a greater generation of micropores at larger burn offs. The generation of mesoporosity is larger with the nitrous oxide treatment, while with the oxygen treatment it remains almost constant. The micropore and supermicropore volumes increase with the burn off, the nitrous oxide treatment producing the largest increase. The different treatments produce an increase in the micropore size, as gasification evolves, being most noticeable for the carbons treated with nitrous oxide. These results show that

the reactive atmosphere plays an important role in the porosity generation [6, 7].

The nitrous oxide treatment produces very stable catalysts in nitrogen atmosphere. There is an agreement with the observations made by Biniak [8] regarding carbons treated in an ammonia gaseous flow, suggesting that nitrogen atoms are incorporated into the superficial carbon layers producing a better thermal stability. Carbons treated in hydrogen are more stable in thermogravimetry tests in nitrogen, while the sample CO/600 shows less stability (figure 1). The stability in tests under nitrogen atmospheres does not depend on the textural modification induced by the oxidative treatment but on the surface chemistry. The oxygen treatment could induce specific surface groups which easily decompose with the increase in temperature, and it is more evident for higher burn offs; on the other hand, the nitrous oxide treatment could give rise to the formation of more stable surface groups.

The gasification of the carbons starts at around 400°C and is independent of the burn off, since similar profiles were observed. Figure 2 shows the characteristic peak maxima temperatures in TPO spectra (T<sub>max</sub>) against burn off. The carbons treated in oxygen present the lowest T<sub>max</sub> in TPO spectra, the lowest one corresponding to the carbon with the greater oxidation degree. On the other hand, the carbons treated in hydrogen exhibit higher T<sub>max</sub>, which is an indication of greater stability, while the carbons treated with nitrous oxide present an intermediate behavior with a small increase in the T<sub>max</sub> at higher burn offs.

Table 2 shows the amounts of CO, CO<sub>2</sub> and the ratio CO/CO<sub>2</sub> released, obtained by integration of the areas under the TPD peaks. For the samples treated in oxygen and nitrous oxide, it could be observed that the CO molar flow released increased with burn-off, being more noticeable for the oxygen treatment. In carbons oxidized in nitrous oxide, a slight decrease in the CO<sub>2</sub> molar flow is observed at low burn-off levels, followed by an increase. In the oxygen treatment, the CO<sub>2</sub> molar flow released increases with burn-off, being always larger than the nitrous oxide treatment. For the hydrogen atmosphere treatment, a decrease in CO and CO<sub>2</sub> molar flow released is observed as burn-off increases. The CO/CO<sub>2</sub> ratio increases for treatments in oxygen and nitrous oxide, being slightly larger for the last one. The molar flows, for CO and for CO<sub>2</sub> released in TPD tests, are associated with surface oxygen groups due to oxidative treatments, mainly anhydrides, lactones, phenols and carbonyl/quinones [9], while hydrogasification produced a sharp decrease in those oxygen groups.

## Conclusions

The different treatments induce textural and surface chemistry changes in activated carbons which may be useful for catalyzing the oxidative dehydrogenation reaction of isobutane under study.

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Table 1. Carbon Characterization

Sample	Proximate Analysis		Elemental Analysis					B.O %	Textural Characterization				
	% m/m, daf		%m/m						BET	W <sub>01</sub>	W <sub>02</sub>	S <sub>meso</sub>	L <sub>μ</sub>
	V.M.	F.C	C	H	N	S	O		m <sup>2</sup> /g	cm <sup>3</sup> /g	cm <sup>3</sup> /g	m <sup>2</sup> /g	nm
CORIG	8.70	91.30	93.21	0.28	0.56	0.84	5.11	1048	0.364	0.032	126	0.96	
CN/180	11.80	88.20	92.73	0.23	0.23	0.67	6.14	10.06	1180	0.407	0.049	139	1.13
CN/360	12.43	87.57	90.48	0.19	0.27	0.55	8.51	12.83	1210	0.414	0.051	153	1.16
CN/600	14.03	85.97	90.02	0.31	0.94	0.68	8.05	22.50	1322	0.443	0.076	180	1.42
CO/360	13.77	86.23	89.75	0.30	0.61	0.63	8.71	8.30	1133	0.393	0.042	128	1.03
CO/600	17.60	82.40	90.05	0.30	0.60	0.42	8.63	19.19	1206	0.415	0.064	130	1.20
CH/180	3.85	96.15	97.55	0.28	0.28	0.10	1.79	6.05	1099	0.382	0.041	120	1.00
CH/360	3.08	96.92	96.56	0.26	0.37	0.01	2.80	7.09	1120	0.389	0.039	121	1.05

V.M: Volatile Matter; F.C: Fixed Carbon

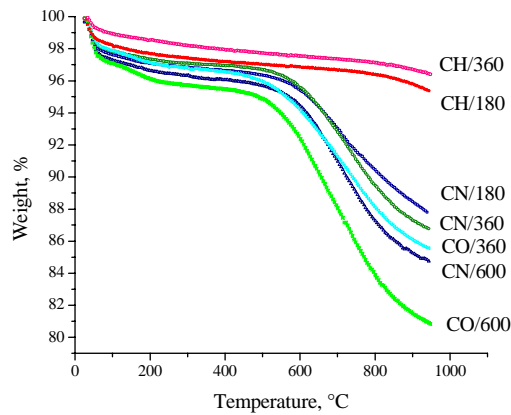


Figure 1. TG curves in nitrogen of the treated carbons

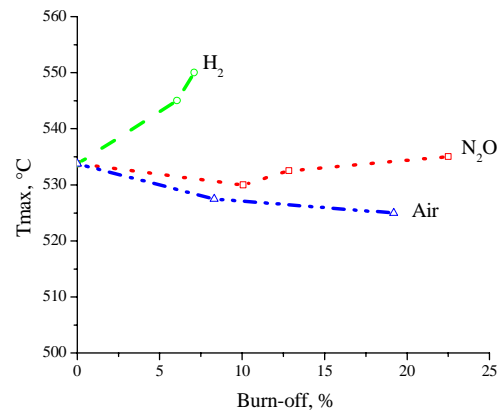


Figure 2. Temperatures of peak maxima in TPO

Table 2. Amounts of CO and CO<sub>2</sub> released, obtained by integration of the areas under TPD peaks

Sample	Burn-Off, %	CO, μmol/g	CO <sub>2</sub> , μmol/g	CO/CO <sub>2</sub>
CORIG		527	235	2.24
CN/180	10.06	1757	205	8.57
CN/360	12.83	2093	211	9.94
CN/600	22.50	2817	300	9.39
CO/360	08.30	2297	286	8.04
CO/600	19.19	3134	370	8.46
CH/180	06.05	223	118	1.89
CH/360	07.09	162	97	1.68