

# OXIDATION OF ISOBORNEOL OVER CARBON CATALYSTS

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## Introduction

Functionalised activated carbons can be used as catalysts in the oxidative dehydrogenation of alkanes (ODH) [1]. When ODH is carried out in the gas phase, it is known that the oxygen atoms of the functional groups on the carbon's surface are responsible for the ODH while the role of the gaseous oxygen of the feed is to reoxidize those functional groups [2]. Aliphatic alcohols undergo dehydration and/or ODH over activated carbons [3].

Camphor is a product of industrial interest which is usually obtained by oxidation of isoborneol. In this work the results of the ODH of isoborneol over functionalised carbons with different surface chemical natures, in the gas and in the liquid phases, are presented

## Experimental

Catalyst samples were prepared using a commercial carbon (NORIT, GAC) as starting material. This material was subjected to the following treatments: N<sub>2</sub>O at 500°C during 1 hr (sample C1); HNO<sub>3</sub> 5 M at room temperature, during 1 hr, followed by washing until neutral pH (sample C2); H<sub>2</sub>O<sub>2</sub> 5M at 100°C, during 1 hr followed by washing until negative peroxide test (sample C3); air at 750°C during 1 hr (sample C4); He at 800°C during 1 hr, followed by O<sub>2</sub> at 300°C during 1 hr (sample C5).

XPS analysis were performed on a XSAM800 (KRATOS) X-Ray Spectrometer. TPD analysis were carried out on a MICROMERITICS TPD/TPR 2900 instrument, being the evolution of CO, NO and CO<sub>2</sub> monitored by mass spectrometry. Textural characterization was performed by nitrogen adsorption at 77 K on a Micromeritics ASAP 2010 V1.01 B instrument. The contents of oxygenated surface groups were also evaluated by titration according to the method of Bohem [4].

The reaction of isoborneol in the gas phase was conducted in a fixed-bed flow type reactor working at atmospheric pressure, using nitrogen as carrier gas, at 150°C, using 0.6 g of catalyst, isoborneol and oxygen partial pressures of 3.39 hPa and an 504.8 hPa, respectively. Isoborneol was fed at a space velocity of 1090 g h mol<sup>-1</sup>.

In the liquid phase the reaction was conducted in a batch reactor, at 55°C under stirring. The reactor was loaded with 0.25 g of isoborneol (Aldrich), 0.25 g of catalyst, 25 ml of acetone (Riedel-de Haën) and 2,5 ml of hydrogen peroxide (30 %, Merck). Analysis were performed by gas chromatography on KONIK HRGC 3000 instrument.

## Results and discussion

The results of XPS (table 1) suggest that all treatments lead to the formation of carboxylic and alcoholic or ketonic functional groups on the carbon surface. However, while the treatment with HNO<sub>3</sub> (C2) leads to the highest content of carboxylic groups, by treatment with O<sub>2</sub> (C5) or N<sub>2</sub>O (C1), the alcoholic (probably phenolic) group is dominant.

These results are in good agreement with the TPD profiles of the carbon samples (figure 1-A, B and C). While the carbon treated with HNO<sub>3</sub> exhibits a low temperature band of desorption of CO<sub>2</sub> (250 - 350°C), usually assigned to carboxylic groups [5,6], that band is not observed for the samples treated with N<sub>2</sub>O or O<sub>2</sub> (figure 1-A). On the other hand, the sample treated with N<sub>2</sub>O exhibits a band of desorption of CO (figure 1-B) at a lower temperature range (400 to 550°C) than the sample treated with O<sub>2</sub> (550 to 900 °C). Probably, the treatment with N<sub>2</sub>O leads to a more unstable structure due to the nitration or some complexation of N<sub>2</sub>O to the aromatic rings of the carbon, occurring simultaneously with the formation of the functional groups above mentioned. However, by XPS, the main observation is the destruction of the surface aromaticity. The carbon gasification with N<sub>2</sub>O is well known [7]. Therefore, the loss of aromaticity of the outer layer of the carbon particle is expectable.

The main products of the reaction of isoborneol on the carbon surface in the presence of O<sub>2</sub> in the gas phase, or H<sub>2</sub>O<sub>2</sub> in the liquid phase, are camphene and camphor. While camphene is formed by the acid catalyzed dehydration of isoborneol, camphor is formed by its oxidative dehydrogenation.

When the reaction is carried out in the gas phase, in the presence of oxygen, the reaction product is dominated by camphene. The best selectivity to camphor is about 10% and is only achieved with the carbon sample treated with O<sub>2</sub> at 300°C (figure 2), although this is the sample exhibiting the lowest activity. With all the other catalyst samples camphor is only formed as traces. This is a consequence of the high acidity of those catalyst samples as observed by titration. That acidity is due to the presence of carboxylic acid groups as suggested by the TPD profiles for all carbon samples except for those treated with O<sub>2</sub> or N<sub>2</sub>O. Although the content of carboxylic groups in the sample treated with N<sub>2</sub>O is low, this sample exhibits the highest acidity because not only this sample bears the highest content in alcoholic groups (probably phenolic) but also because their acid strength is probably enhanced by the nitration of the aromatic rings, as suggested by the band of desorption of NO shown in the TPD profile (figure 1-C). However, this modification must arise deeply in the pores, since by XPS the amount of nitrogen

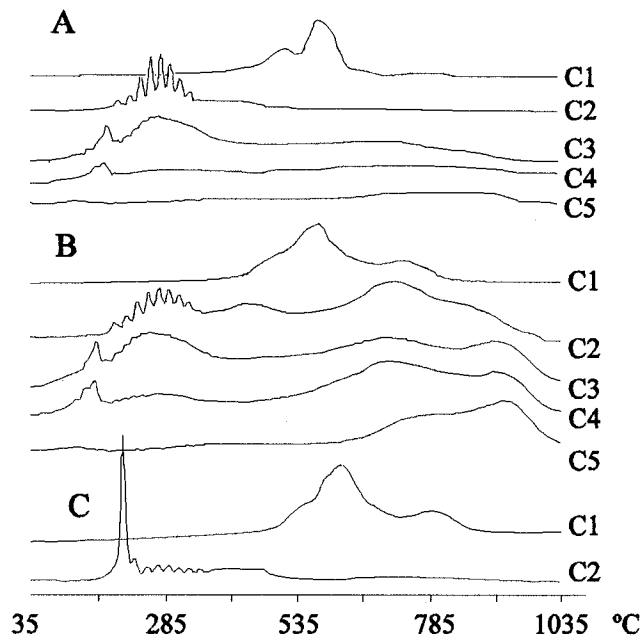
decreases relatively to the parent carbon. Also as referred above, the surface aromaticity completely disappears. Textural characterization showed that no significant changes in the surface area were observed for the different catalyst samples. Nevertheless, sample C1 exhibited a much smaller micropore area. Therefore, only in the case of the carbon treated with O<sub>2</sub> is the surface acidity low enough to allow for the oxidation reaction of isoborneol.

In the liquid phase the only catalyst sample tested was the carbon treated with H<sub>2</sub>O<sub>2</sub>. The main product is, in these conditions, camphor (figure 3). The dehydration reaction of isoborneol is now inhibited, probably due to the lowering of the acid strength of the carboxylic and phenolic groups as a consequence of solvation.

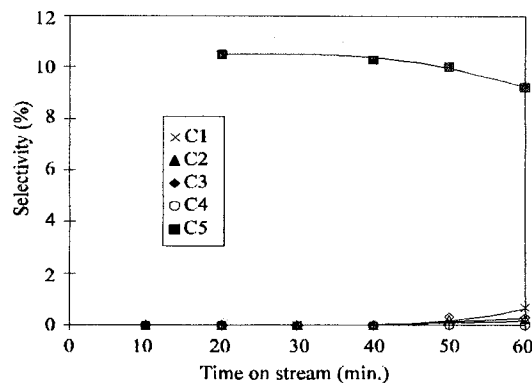
**Table 1.** Area (%) of the relevant peaks of activated carbons reported to 100% C<sub>1s</sub>, 100% O<sub>1s</sub> and 100% N<sub>1s</sub>

Sample	Csp2	Csp3	COR	C=O	COOR
C1	61.1	-	24.1	2.5	1.0
C2	44.1	23.6	12.0	6.1	3.2
C3	46.8	23.9	14.4	2.8	1.2
C4	46.6	24.4	12.8	3.3	1.6
C5	46.7	24.0	13.3	3.5	1.5

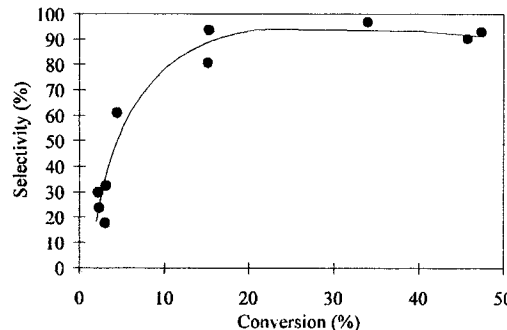
Sample	Aromatic C=O	CO, COH, COOR, C=O	Phenol, COOR
C1	30.8	31.9	26.6
C2	24.5	45.9	16.1
C3	23.2	46.1	15.9
C4	16.2	38.5	18.3
C5	23.0	36.9	28.0



**Figure 1.** TPD profiles of the catalyst samples. A - CO<sub>2</sub>; B - CO; C - NO.



**Figure 2.** Oxidation of isoborneol in the gas phase. Selectivity to camphor



**Figure 3.** Oxidation of isoborneol in the gas phase. Selectivity to camphor

## Conclusions

In the gas phase reaction conditions was observed that very acidic surfaces seem to promote dehydration of isoborneol to camphene.

Oxidation to camphor seems to be favored by the presence of phenolic and quinone groups.

In liquid phase, sample C3 exhibit the highest selectivity to camphor.

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