

TPD OF ACTIVATED CARBON MATERIALS FOR CATALYTIC APPLICATIONS

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INTRODUCTION

Carbon materials are finding an increasing number of applications in catalysis, either as supports for the active phases, or as catalysts on their own. Their performance is determined both by their texture and surface chemistry [1]. In the case of activated carbons, the texture may be adapted to suit the situation by adequate choice of the activation procedure [2]. In particular, it is possible to prepare carbons with different proportions of micro, meso and macropores.

On the other hand, the nature and concentration of surface functional groups may be modified by suitable thermal or chemical post-treatments, such as oxidation in the gas or liquid phase, and thermal treatments under inert or reactive atmosphere. Carboxyl, carbonyl, hydroxyl, quinone, and lactone groups, have been identified on carbon surfaces [3,4].

In this work, we have used activated carbons from different origins and submitted to different treatments in order to obtain catalysts with different surface properties. In particular, we examined the oxydative dehydrogenation of ethylbenzene to styrene, since activated carbons and carbon molecular sieves have been reported to be good catalysts for this reaction [5,6]. In these studies, catalyst performance was mainly correlated with the texture of the catalyst.

However, when this reaction is carried out in the presence of inorganic oxides, it has been found that a carbonaceous overlayer is formed initially, which seems to be the true catalyst; moreover, surface groups of the quinone type have been proposed as the active sites [7,8]. Therefore, we have tried to interpret the activity and selectivity of the carbon catalysts in terms of their surface chemistry determined by temperature programmed desorption, or TPD. This technique is able to provide both qualitative and quantitative informations on the surface oxygen complexes which determine the properties of the material.

EXPERIMENTAL

A NORIT[®] RX3 Extra activated carbon was used as supplied and after two types of oxidation treatment: with 5% O₂ at 723 K, and with 5M or 0.2M nitric acid. Other carbons were produced in the laboratory: from coconut shells, after carbonization under inert atmosphere at 1073 K and i) activation by steam at 1173 K (41.2% burn-off) or ii) by carbon dioxide at 1073 K catalysed with 7% KOH to a burnoff of 5.8%; iii) from pinewood by chemical activation with H₃PO₄ at 623 K.

The TPD runs were carried out in a set-up made up of a U-shaped tubular micro-reactor, placed inside an electrical furnace. The mass flow rate of the helium carrier gas (69 µg/s) and the heating rate (5K/min) of the furnace were controlled with appropriate units. The amounts of CO and CO₂ desorbed from the carbon sample were monitored with a SPECTRAMASS[®] Dataquad quadrupole mass spectrometer.

The catalytic tests were carried out with an AUTOCLAVE ENGINEERS[®]BTRS reactor, working with a mixture of air and ethylbenzene in the proportions of 42:1 at 623 K and with a space time of 0.2 s. The effluent composition was monitored on-line with a TREMETRICS[®] gas-chromatograph with an FID detector and a 15 m capillary column of DB-5ms.

RESULTS AND DISCUSSION

Figure 1 shows the TPD of CO₂ and CO, respectively, of the same activated carbon after different treatments. It is shown that nitric acid oxidation increases the CO₂ evolution at low temperatures, while the oxidation in the gas phase induces both a CO and a CO₂ peak at higher temperatures. These results are consistent with an increase in carboxylic acid groups after nitric acid treatment, whereas gas phase oxidation increases anhydride, phenol, carbonyl, quinone or lactone surface groups.

In a similar way, the materials activated under different conditions exhibit distinct TPD patterns which clearly demonstrate their different surface chemistry.

The method does not distinguish between the different surface complexes that decompose yielding CO at high temperatures; nevertheless, the results indicate that gas phase oxidation is a treatment with a good chance of increasing the concentration of the required quinone groups to catalyse the oxydative dehydrogenation of ethylbenzene to styrene.

The results obtained with NORIT® carbons as catalysts before and after oxidation are shown in Table 1. It is clear that gas phase oxidation increases substantially the yield of styrene, in contrast to the nitric acid treatment.

CONCLUSIONS

It has been shown that gas phase oxidation of carbon increases the concentration of the surface complexes that decompose by releasing CO at high temperatures, increasing at the same time the catalytic activity of the material for the oxidative dehydrogenation of ethylbenzene. On the other hand, liquid phase oxidation increases

the concentration of carboxylic groups, which play an important role in the preparation of carbon supported metal catalysts [9].

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Table 1- Catalytic results for the oxidative dehydrogenation of ethylbenzene

Carbon NORIT®	original	HNO ₃ oxidised	O ₂ oxidised
Ethylbenzene conversion (%)	16	26	34
Styrene selectivity (%)	30	33	50
Activity (μmol/s/g)	0.6	1.0	1.4

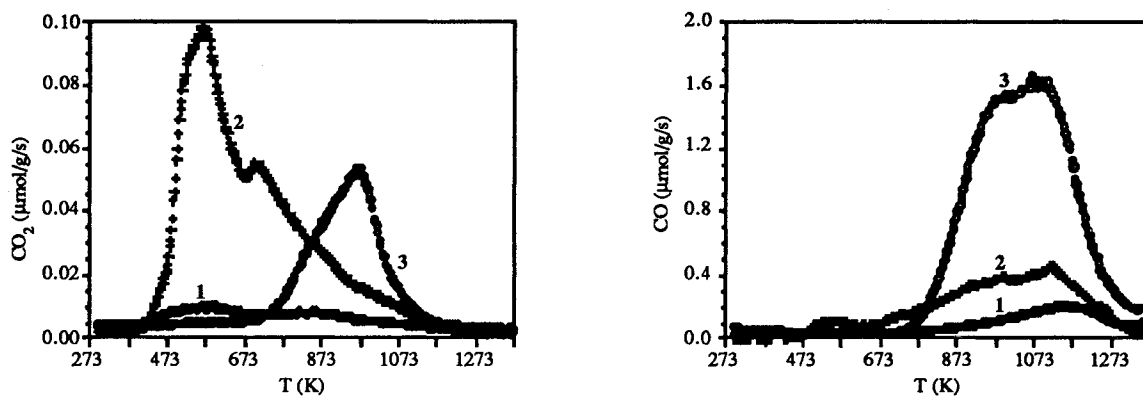


Figure 1 - TPD spectra of CO₂ (left) and CO (right) of the RX3 ® carbon before and after oxidation: 1- original; 2- oxidised with HNO₃ 5M (6 hours); 3- oxidised with 5% O₂ (6 hours).