

Investigation of styrene production over carbon catalysts using high-pressure XPS.

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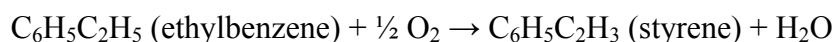
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Introduction.

High-pressure in situ X-ray photoelectron spectroscopy is a useful technique for the elucidation of active phases under reaction conditions [1]. Our reaction of interest was the oxidative dehydrogenation (ODH) of ethylbenzene to styrene:



This is an important process in the petrochemical industry. It is well known that carbon materials such as activated carbons [2], activated carbon fibres, carbon blacks and more recently carbon nanotubes and onion-like carbons are good catalysts in the oxidative dehydrogenation of ethylbenzene to styrene. In the literature, it is speculated that carbonyl and quinone groups play the role of active phase in the oxidative dehydrogenation [3,4] and recent results at a pressure of 1 atm [5] support this idea. The previously mentioned experiments [5] (quasi in-situ) are not real in-situ experiments because the sample was analyzed after reaction but not during reaction. The goal of the proposed experiments was to obtain photoemission spectra of a catalyst's surface under working conditions and it must be pointed out the novelty of the experiments performed, it is the first time that this type of experiments has been applied to the oxidative dehydrogenation of ethylbenzene to styrene.

Experimental.

In the present study, we employed different carbon materials to study changes on the surface during oxidative dehydrogenation of ethylbenzene to styrene by high pressure XPS. The samples used were: a graphite (DFP-1, Poco Graphite), DFP-1 oxidized by HNO₃ (65%), carbon fibres (Donacarlo S-241, Osaka Gas Co., Ltd) oxidized by nitric acid, activated carbon fibres and activated carbon fibres oxidized by nitric acid. The catalytic activity of the different samples was measured by a quadrupole mass spectrometer and a proton-transfer reaction mass spectrometer (PTR) coupled to the XPS equipment. Temperature ranged from 325 to 500°C, being 325°C the most widely-used temperature. A stoichiometric molar ratio of ethylbenzene/O₂ = 2 and a total pressure of 0.25mbar were employed. The energies of the photons were calibrated by calculation of the Fermi level of a gold film. Samples mainly contained carbon and oxygen, and some of them contained also nitrogen. In order to separate the gas phase and surface contributions to the C1s and O1s peaks, a potential of 150V was applied to the nozzle.

Results and discussion.

In spite of the high pressure employed (0.25mbar) and the subsequent attenuation of the XPS signal, XPS spectra with a good intensity were obtained.

All the above-mentioned samples showed some styrene production, the higher the surface area and oxygen functional groups content, the higher was the styrene production. Results for the graphite DFP-1 oxidized by HNO_3 are shown as a representative example of the experiments carried out. Sample was mounted in the reaction chamber and it was heated up to 400°C in vacuum losing an important amount of oxygen on the surface.

Figure 1 shows the response of the quadrupole mass spectrometer for the $m/e = 104$ (related to styrene) versus time and at different temperatures (400 and 500°C). Oxidative dehydrogenation starts at around 320°C and increases with reaction temperature. Therefore styrene production at 0.25mbar is proved.

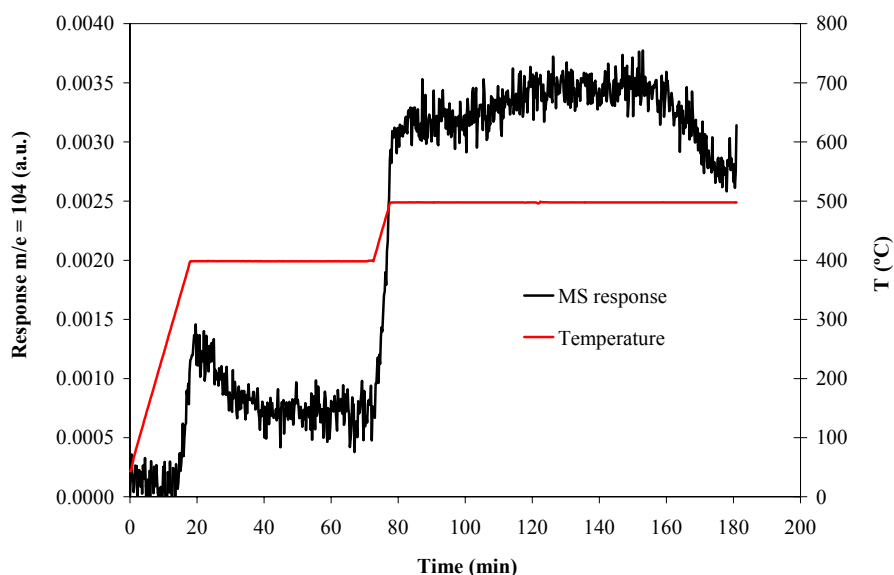
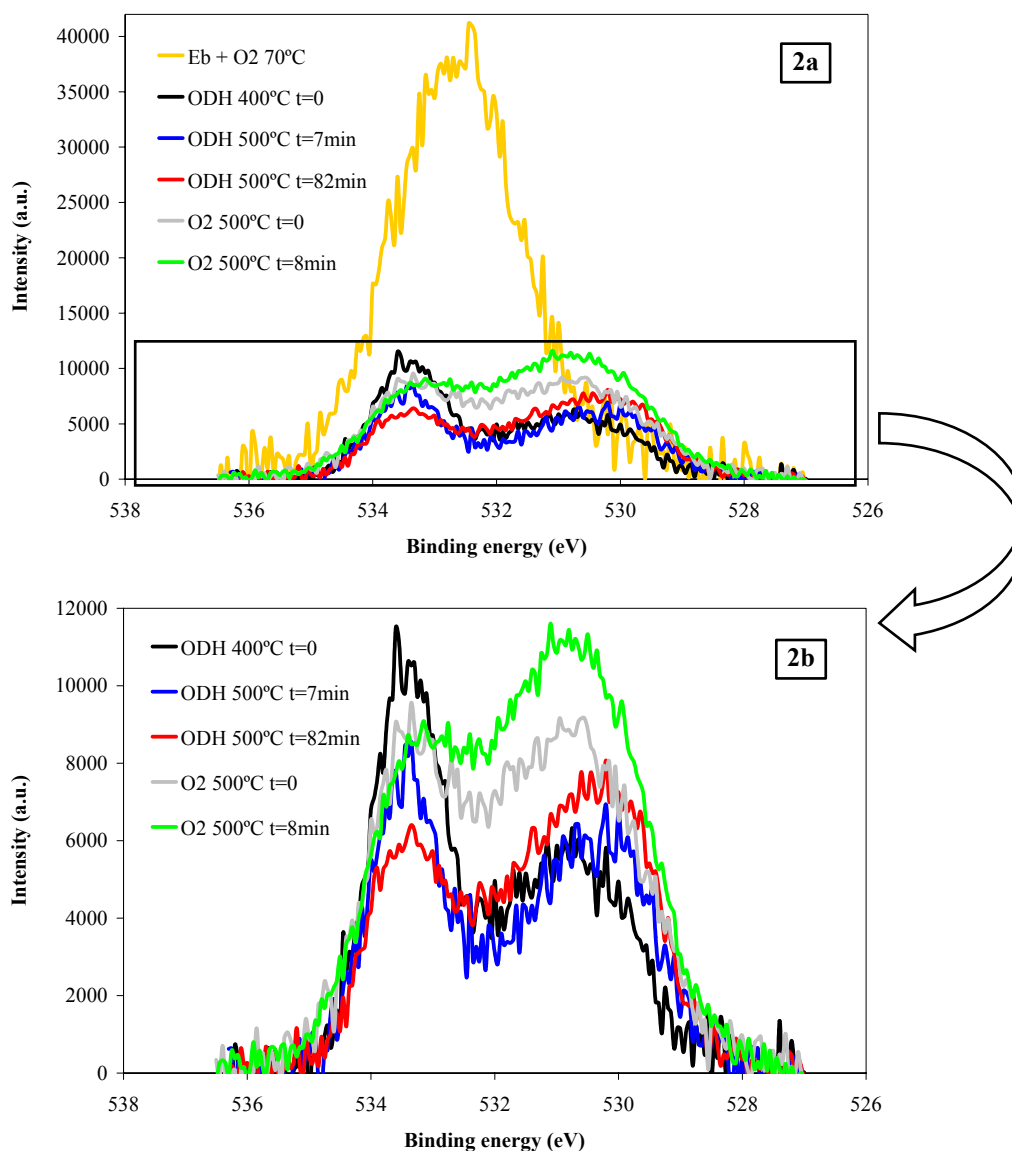


Figure 1. MS response for $m/e = 104$ with time and temperature.

Figures 2a and 2b contain O1s spectra of the sample under different reaction conditions. A Shirley type background has been used and the intensity has been normalized to the beam intensity. XPS spectra areas have been corrected considering that C1s peaks have the same area in order to compare O1s peaks directly.

It can be observed that the sample under an atmosphere of ethylbenzene (Eb) and O_2 at 70°C (orange line) has a high amount of oxygen groups on the surface. After, heating the sample up to 400°C (black line), oxidative dehydrogenation of ethylbenzene to styrene takes place and a pronounced decrease in the O1s peak is observed. Oxygen groups at around 530eV are practically not affected and, on the contrary, the rest of the groups decrease considerably. This fact can be explained by desorption of oxygen groups and by chemical transformation of oxygen groups in presence of O_2 . When the temperature of the ODH reaction is increased until 500°C and kept constant for a period of time (blue and red lines), the peak at around 533eV decreases, the peak at around 530eV is shifted to lower binding energies and the intensity increases with increasing the reaction time. The decrease of the peak at 533eV can be ascribed to a stronger oxidation of groups C-O towards C=O (530eV). In the same way, long reaction time (red line) favours oxidation of oxygen groups and increases the peak at 530eV at the expense of the peak at 533eV . After that, the sample was heated in vacuum at 500°C for several minutes and, then, O_2 was introduced at 500°C (grey line). As it can be observed, O_2 atmosphere produces a higher amount of oxygen groups at around 533eV than ODH at the same temperature but after a shorter period of time. It seems that the aforesaid groups (carbonyl) are involved in the ODH reaction. In agreement with previous results at 1 atm [5], there are mainly two peaks involved (530 and 533eV) in the ODH.



Figures 2a & 2b. XPS O1s spectra under different atmospheres and temperatures of the graphite DFP-1 oxidized by HNO₃.

Acknowledgements.

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