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Oxygen functional groups involved in the styrene production reaction detected by quasi in situ XPS

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Abstract

In this work, the oxidative dehydrogenation (ODH) of ethylbenzene to styrene reaction over an activated carbon felt was studied by experiments of mass spectrometry coupled to a quasi in situ XPS system. These experiments permit to deepen into the mechanism of the aforementioned reaction. The results obtained allow us to conclude that carbonyl-quinone and hydroxyl groups are involved in the ODH. The amount of both types of oxygen groups increases when the ethylbenzene conversion to styrene increases. Therefore, the reaction seems to take place through the carbonyl-quinone/hydroxyl and styrene/ethylbenzene redox couples, confirming that carbonyl-quinone are the active phase in this oxidative dehydrogenation.

Keywords: Activated carbon fibres; Ethylbenzene; Styrene; Oxidative dehydrogenation; Oxygen groups; XPS

1. Introduction

Styrene is an important chemical extensively used in the manufacture of polymers, copolymers and reinforced plastics, like polystyrene (which accounts for over 50% of the total production of styrene), acrylonitrile–butadiene–styrene (ABS) resins, styrene–acrylonitrile resins (SAN), styrene–butadiene rubber (SBR), styrene–butadiene latex, unsaturated polyester resins, etc. Styrene is produced by two methods: as a co-product of propylene oxide production and by dehydrogenation (DH) of ethylbenzene catalysed by potassium-promoted iron oxides [1] according to reaction (1).

$$\text{DH}: \quad C_6H_5C_2H_5\ (\text{ethylbenzene}) \rightarrow C_6H_5C_2H_3\ (\text{styrene}) + H_2, \quad \Delta H^0_{298\,K} = +117.6\,\text{KJ/mol} \tag{1}$$

Oxidative dehydrogenation (ODH) of ethylbenzene is a third possibility to produce styrene (see reaction (2)).

$$\text{ODH}: \quad C_6H_5C_2H_5 + \tfrac{1}{2}O_2 \rightarrow C_6H_5C_2H_3 + H_2O, \quad \Delta H^0_{298\,K} = -124.3\,\text{KJ/mol} \tag{2}$$

Although the research on the DH reaction is more extensive than on ODH, the interest on the last process is gaining attention and it is the subject of numerous studies nowadays.

The ODH process has some advantages compared to the non-oxidative method, caused by the endothermic character of the DH reaction and the exothermic nature of the ODH. Consequently, lower temperature is needed to carry out the ODH reaction since the hydrogen oxidation generates the energy needed for the endothermic dehydrogenation; additionally, the hydrogen is removed from the reaction and the styrene yield increases.

Carbon materials such as activated carbons [2–9], activated carbon fibres [10,11], carbon blacks [12,13] and, recently, carbon nanotubes [14] and onion-like carbons [15] are good catalysts for the oxidative dehydrogenation of ethylbenzene to styrene. Those materials contain carbon atoms with sp^2 hybridisation and oxygen functional groups,

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which favour the reaction. During the oxidative dehydrogenation of ethylbenzene catalysed by carbon, a continuous polymer organic deposit (POD) takes place [16]. This POD is known to be also active and its presence increases the catalytic activity of some catalysts, for instance Al_2O_3 [17,18]. The POD has a non-well defined composition; it is proposed to consist of a polyaromatic structure (C sp^2) with a high proportion of oxygen functional groups at the edge of the rings [19].

It is speculated that the oxygen groups (carbonyl and quinone) are the active phase in the oxidative dehydrogenation reaction [7,18]. The mechanism proposed consists of a red-ox reaction between the pairs carbonyl/hydroxyl and styrene/ethylbenzene [20–22]. Oxygen gas added in the feed regenerates the active phase by oxidation of the hydroxyl to the carbonyl. Although this is a reasonable mechanism, it is a speculation since the nature of the oxygen groups formed has not been identified under reaction conditions. Thus, the objective of this work is to gain insights into the nature of the oxygen groups participating in the ODH reaction catalysed by a porous carbon, by experiments of mass spectrometry coupled to a quasi in situ XPS system [23,24].

2. Experimental

An activated carbon fibre felt ''KF-1500'' developed by Toyobo Co., produced by using cellulosic fibres as the base material, was employed as catalyst.

The characterisation of the porosity of the activated carbon was done by physical adsorption of N_2 at −196 °C and CO_2 at 0 °C (Quantachrome, Autosorb-6). The samples were outgassed at 250 °C under vacuum for 4 h. Nitrogen adsorption was used to obtain the BET surface area and the Dubinin–Radushkevich (DR) micropore volume (i.e., volume of pores of size below 2 nm). Carbon dioxide isotherms were employed to obtain the DR_{CO_2} micropore volumes, which correspond to pores of size below 0.7 nm [25].

The XPS experiments were carried out in a modified LHS/SPECS EA200 MCD system equipped with facilities for XPS (Mg Kα 1253.6 eV, 168 W power) measurements. For the XPS measurements a fixed analyser pass energy of 48 eV was used resulting in a resolution of 0.9 eV FWHM of the Ag $3d_{5/2}$ peak. The binding energy scale was calibrated using Au $4f_7/_2$ = 84.0 eV and Cu $2p_3/_2$ = 932.67 eV. XPS spectra areas have been corrected considering that C_{1s} peaks have the same area in all the samples. The sample was mounted on a stainless steel sample holder. The pressure of the UHV analysis chamber was below 10^{-10} mbar. Quantitative data analysis was performed by subtracting Shirley background [26] and using empirical cross sections [27]. Binding energy of the peak C_{1s}, corresponding to graphitic carbon, was referenced at 284.6 eV.

For the tests of oxidative dehydrogenation of ethylbenzene, the amount of sample used was 9 mg in all the cases. The composition of the carrier gas was 21% O_2 and 79% N_2 and the total flow was 30 or 40 ml/min. The carrier gas passes through a saturator with liquid ethylbenzene at 25 °C; in this way, a flow of gas containing a 1.26% (v/v) of ethylbenzene is obtained. The temperatures used in the catalytic experiments were 350, 375 and 400 °C and the pressure about 1 atm. A heating rate of 12 °C/min was employed and then about 30 min are required to reach the final temperature. The analysis of the gases and vapors was done in a quadrupole mass spectrometer (MS) Prisma (Balzers) equipped with a leak valve. These experiments were done in a reaction chamber (Fig. 1) and the treated sample was transferred to the XPS analysis chamber avoiding the contact with air. The mass spectrometer signal was corrected for the minor changes occurring during the periods of the experiments and for fragmentation. Also, the signals were calibrated with a known concentration of styrene. The known concentration of styrene is obtained by passing a carrier gas (21% O_2 and 79% N_2) through a saturator with styrene at 25 °C. Concentration is calculated by using styrene vapour pressure at 25 °C.

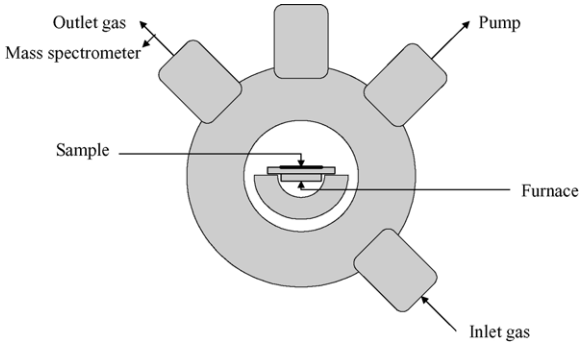

Fig. 1. Scheme of the reaction vessel.

3. Results and discussion

3.1. Characterisation of porosity

The nitrogen isotherm (Fig. 2) is of type I indicating that the sample is essentially microporous. Additionally, the

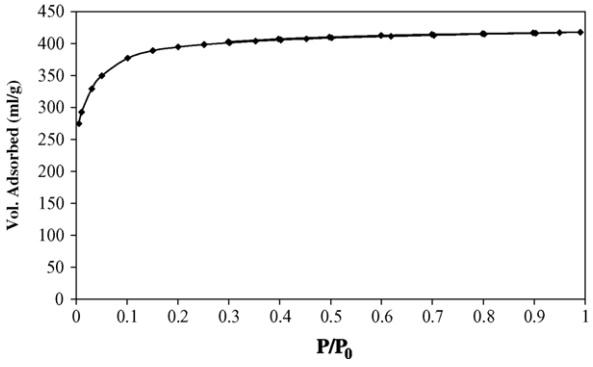

Fig. 2. Nitrogen adsorption and desorption isotherm of the sample KF-1500 at −196 °C.

Table 1
Porosity results of the sample KF-1500

Sample	KF-1500
S_{BET} (m^2/g)	1361
$V_{DR\,N_2}$ (ml/g)	0.65
$V_{DR\,CO_2}$ (ml/g)	0.45

narrow knee of the isotherm shows that the material has a narrow micropore size distribution. The KF-1500 sample has a high surface area and micropore volumes (Table 1), demonstrating that it has an important development of microporosity.

3.2. XPS quasi in situ and catalytic experiments

3.2.1. Influence of the reaction temperature

We tested three reaction temperatures. Fig. 3 contains the ethylbenzene conversion to styrene at different temperatures and using a flow of 40 ml/min, followed by MS. The recording of the MS data was started at time zero (Figs. 3 and 7). Styrene detection starts when the temperature of the sample is close to 290 °C (around 1300 s of time). Around 2500 s, after reaching the desired temperature, are needed to reach the steady state because the volume of the reaction vessel is considerably large (about 260 ml). It can be observed that the styrene formation increases with reaction temperature, and that there is a significant increase in the concentration when the reaction occurs at 400 °C. At the steady state the ethylbenzene conversion to styrene at 400 °C is more than twice than that obtained at 350 °C. It must be pointed out that there is an important production of CO_2 under these experimental conditions (Fig. 4). CO_2 mainly comes from the oxidation of both ethylbenzene and activated carbon fibres.

Samples treated at different temperatures during the ODH reaction were analysed by XPS. The C_{1s} and O_{1s} regions of the XPS spectra were analysed in detail. Fig. 5 contains the C_{1s} spectra for the pristine sample, the one treated in N_2 at 400 °C and those after reaction at different temperatures. All the spectra contain a very intense peak at around 284.5 eV, typical for graphitic carbon [28]. The tail and the shoulder at higher binding energies are related to oxygen functional groups on the carbon surface. The figure reveals that there are no significant differences in C_{1s} spectra between the samples, indicating that the intensity from the functional groups created after the reaction is very weak compared with the strong excitations of C_{1s} electrons and is hardly detectable in C_{1s} spectra.

However, changes in the O_{1s} spectra (Fig. 6) can clearly be detected showing differences between the pristine and those after the ODH reaction at different temperatures. XPS spectra of the samples treated under N_2 (Fig. 8) are compared with samples treated in ODH, since it is well known that carbon samples lose some oxygen groups at low temperatures when are heated [29]. The O_{1s} peak mainly has three contributions that can be interpreted according to the literature on carbon materials (see [30–37]) as: a charged peak (at around 536.6 eV), hydroxyl groups and chemisorbed water (at around 533.5 eV) and carbonyl groups (at around 531.4 eV). It must be noted that the peaks at 531.4 and 533.5 eV increase with the reaction temperature, although the peak at 533.5 eV increases more than the peak at 531.4 eV when it is compared to the pristine sample. The increase in these peaks is more significant at 400 °C, a similar trend to that observed in the ethylbenzene conversion to styrene (Fig. 3).

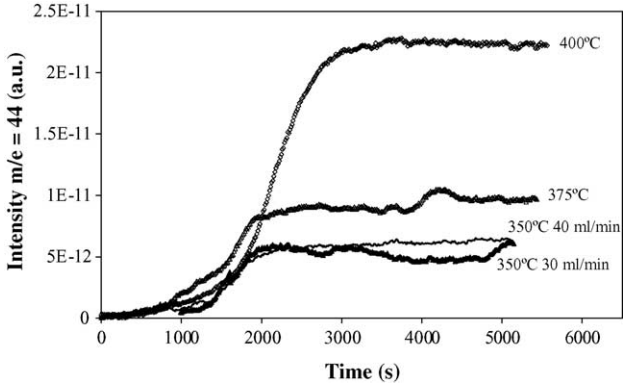

Fig. 4. Variation of the $m/e = 44$ during ODH reaction.

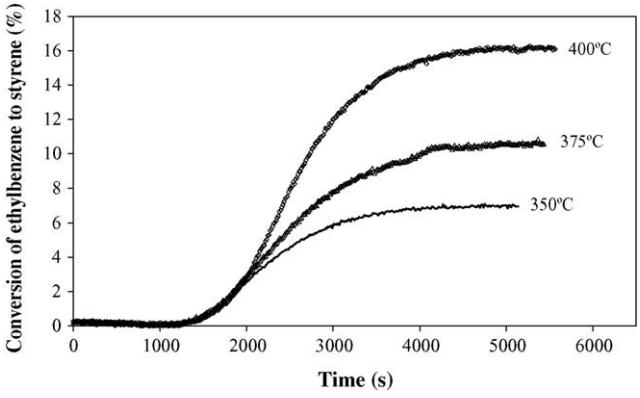

Fig. 3. Ethylbenzene conversion to styrene at 350, 375, 400 °C and 40 ml/min of total flow.

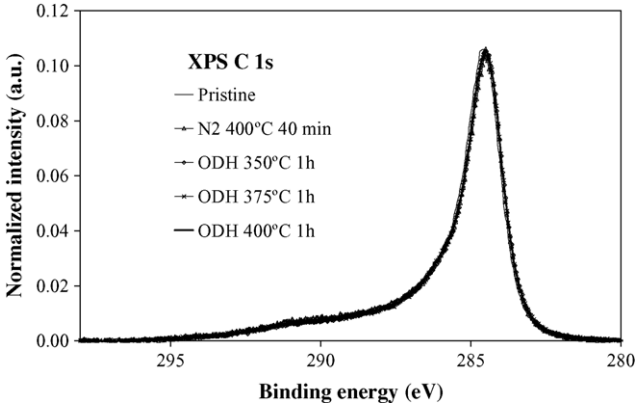

Fig. 5. XPS C_{1s} spectra of samples: pristine, treated at 400 °C in N_2, treated at 350, 375 and 400 °C in ODH, the total flow was 40 ml/min.

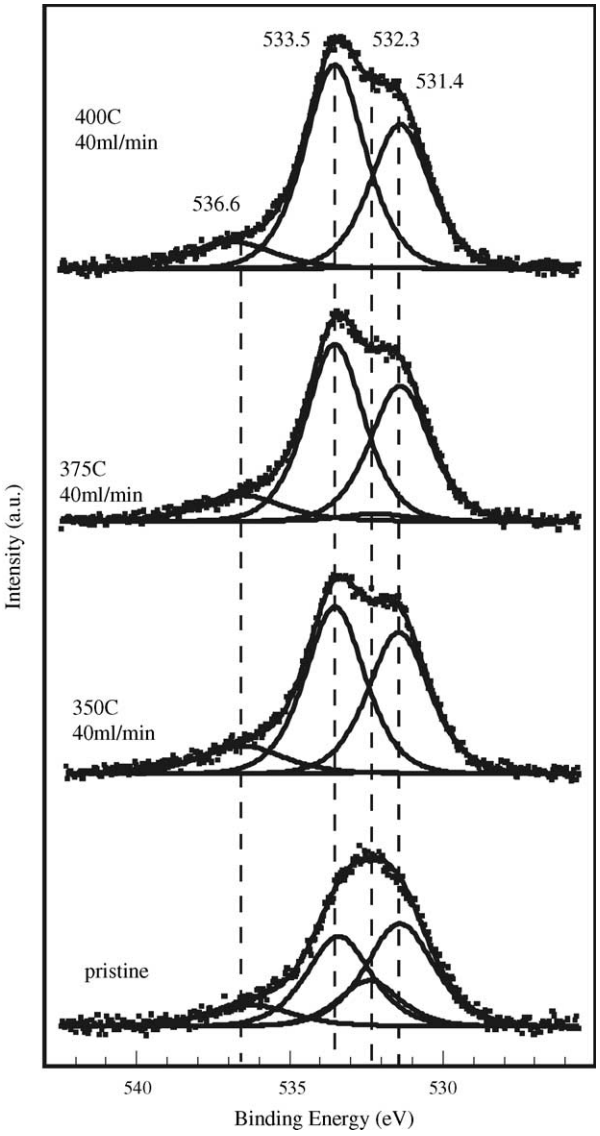

Fig. 6. Deconvolutions of XPS O_{1s} spectra of samples: pristine, treated at 350, 375 and 400 °C in ODH, the total flow was 40 ml/min.

3.2.2. *Influence of the gas flow*

In order to find out how the gas flow influences the oxygen content and functional groups, experiments were performed at the constant temperature of 350 °C and the two flow rates of 30 and 40 ml/min. Fig. 7 contains the ethylbenzene conversion to styrene at the two flows. The experiments reveal that the ethylbenzene conversion towards styrene formation increases with decreasing the flow.

The C_{1s} spectra (not included) obtained for a flow of 30 and 40 ml/min are almost identical, similarly to those included in Fig. 3. However, the O_{1s} spectra (Fig. 8) reveal that there is a significant influence of the gas flow used on both the oxygen content and on the proportion of the functional groups formed. Thus, the peaks at 531.4 and 533.5 eV increase with decreasing gas flow, but the peak at 531.4 eV increases in a higher extent than the peak at

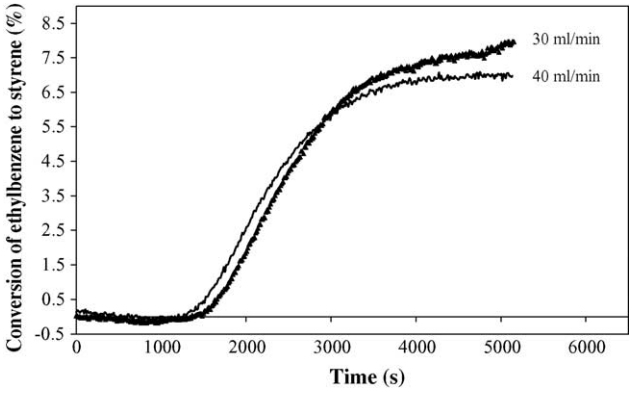

Fig. 7. Ethylbenzene conversion to styrene for 30 and 40 ml/min at 350 °C.

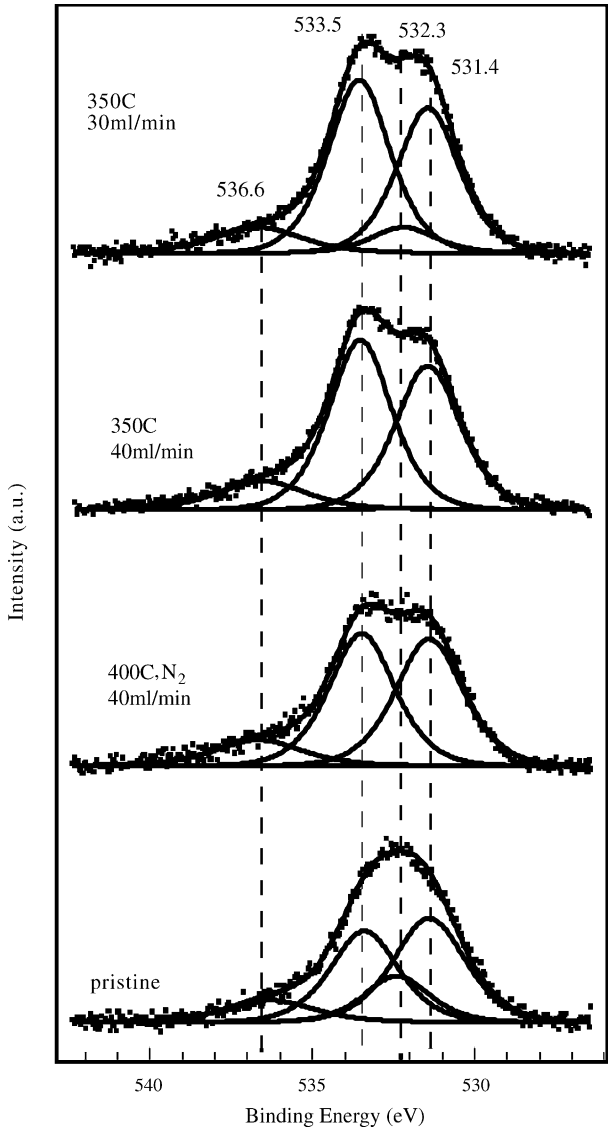

Fig. 8. Deconvolutions of XPS O_{1s} spectra of samples: pristine, treated at 400 °C in N_2, treated at 350 °C in ODH at a flow of 30 and 40 ml/min.

533.5 eV. The high ethylbenzene conversion to styrene is connected with a high intensity of both peaks (531.4 and 533.5 eV) in the O_{1s} spectrum.

All these observations confirm that the reaction mechanism occurs through a red-ox reaction between the couples: styrene/ethylbenzene and carbonyl/hydroxyl. The role of O_2 is to oxidize hydroxyl groups to carbonyl and then complete the catalytic cycle or to oxidize the carbon surface to develop new carbonyl type groups. The relative amount of the oxidized groups (i.e., carbonyl) increases by decreasing the flow. This increase could be explained as follows: lower flow induces higher ethylbenzene conversion to styrene and larger amount of hydroxyl groups are formed. These hydroxyl groups are reoxidized by O_2 towards carbonyl.

Additionally, experiments feeding only ethylbenzene have been carried out. A clear increase in the proportion of OH-containing species compared to carbonyl has been observed. This suggests that carbonyl groups are reduced by ethylbenzene forming styrene. In the absence of O_2 the hydroxyl oxidation does not happen, thus producing a change in the proportion of carbonyl/hydroxyl groups compared to the ODH. This agrees with the conclusions from the ODH experiments.

4. Conclusions

To the best of our knowledge, this is the first time that quasi in situ XPS has been carried out with the oxidative dehydrogenation of ethylbenzene reaction. This technique is specially interesting due to the valuable information provided on the nature of the active surface, considering that the contact with air of the samples after reaction is avoided. The results indicate that carbonyl-quinone and hydroxyl groups are involved in the ODH of ethylbenzene towards styrene. The amount of both type of oxygen groups (carbonyl-quinone and hydroxyl) increases when the ethylbenzene conversion to styrene increases (increasing the temperature or decreasing the flow). Therefore, the reaction seems to take place through the carbonyl-quinone/hydroxyl and styrene/ethylbenzene redox couples, confirming that these oxygen groups are the active sites in the oxidative dehydrogenation.

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