Phosphorous-induced thermal stabilization for carbon-supported SiO$_2$ catalysts in the oxidative dehydrogenation of ethylbenzene to styrene

A strategy to enhance the thermal stability of C/SiO$_2$ hybrids for the O$_2$-based oxidative dehydrogenation of ethylbenzene by P addition is proposed. The preparation consists of the polymerization of furfuryl alcohol (FA) on a mesoporous precipitated SiO$_2$. The polymerization is catalysed by oxalic acid (OA) at 160 $^\circ$C (FA:OA=250). Phosphorous was added as H$_3$PO$_4$ after the polymerization and before the pyrolysis that was carried out at 700 $^\circ$C and will extend the overall activation procedure. The carbon and P loadings slightly alters the textural parameters; the pores retain the cylindrical shape with a fraction of micropores, resembling a coating. The catalytic tests were carried out under limited O$_2$, high EB concentration, and temperature in the range of 425-475 $^\circ$C. The tests show that the P/C/SiO$_2$ hybrids are readily active, selective, and stable in the applied reactions conditions for 60 h time on stream. The comparison with MWCNT reveals that the P/C/SiO$_2$ hybrids are more active and selective at high temperatures (450-475 $^\circ$C), while the difference becomes negligible at lower temperature. Characterization of the spent catalysts shows that P/C/SiO$_2$ hybrids build up substantial coke and due to the overcoking, having pore network restrictions, pore volume, and surface area depletion.
4.1 Introduction

In the petrochemical industry styrene (ST) production is considered one of the major processes; styrene is used principally as a monomer for polystyrene with different grades and as a component in the synthesis of styrene-butadiene co-polymer for automobile tires. ST is industrially over 85 % produced by direct dehydrogenation of ethylbenzene (EB) over a K-promoted Fe₂O₃ catalyst at 580-630 °C using an excess of steam [1]. The major feature of this process is the extremely high selectivity (>96 %), that makes the downstream processing relatively simpler, as compared to other catalytic processes. The (small) amounts of byproducts (benzene, toluene, and hydrogen) have also commercial value. The process suffers, however, from high steam consumption, moderate conversion per pass due to the equilibrium limitations, and high temperatures are required for the endothermic reaction [2]. Remarkable efforts now and in the past have been put in to overcome the equilibrium recycle, reducing the operation temperature, reducing the steam to EB ratio, and replacing steam by oxidants, such as O₂ or CO₂, or combinations thereof. The use of oxidants in this process (ODH route), can in theory and will in practice reduce the reaction temperature as the equilibrium limitation disappears for the case of O₂ or it is improved for the CO₂-based ODH. It is nevertheless not an easy task finding a highly selective catalyst in the presence of an oxidant. This is because EB is also gasified and/or fully oxidized into CO/CO₂ that has no economic value. Besides the selectivity, the ODH process is not commercialized yet due to the limited catalyst stability.

Two types of catalyst families have been proven to be active and selective for EB ODH. Inorganic-based materials such as aluminas [3-8], metal pyrophosphates [9-11], and phosphates [10-20], or P-supported silica [10,21] have been reported as a first class of catalysts. There is a general consensus that the coke deposit generated on the acid sites under these oxidative reaction conditions is more active and selective for the production of ST than the inorganic material itself [3-6,8,22]. In fact, the formation of coke initially improves the activity and selectivity, however, in the long term an excess of carbon deposit leads to catalyst deactivation. Depending on the reactions conditions there is an activation period to achieve pseudo-stationary conditions, i.e. a period of time necessary to achieve full coverage of active coke on the surface, where the conversion and selectivity to styrene achieve both a maximum. We recently showed that for alumina it can be significantly shortened by working at 475 °C instead of 450 °C [8].

The second catalyst family includes carbon based materials, such as activated carbons [23-29], carbon nano-fibers [30-35], onion-like carbon [36,37], diamonds [37,38], and multi-walled carbon nanotubes (MWCNT) [38-42]. These materials are readily active and selective; the reported selectivities lie within 70-90 % that is low to moderate, as compared to the commercial steam dehydrogenation process (>96%). In some cases, the reported selectivity is significantly high, ranging 90-97%, however, in an excess of oxygen [42-44]. The performance and stability of these carbon-based catalytic materials is in general difficult to compare due to large differences in the applied operation conditions. Principally temperature range, EB concentration, space velocity, and O₂:EB vary significantly among the reported literature. We have recently compared, under identical and relevant ODH conditions, various types of carbon-based catalysts, ranging from conventional to nano-structured carbons [45]. It was found that nano-structured MWCNT is the most stable material; the structure resists the reaction conditions showing an EB conversion of ca. 30% (but deactivating) with a steady selectivity of ca. 80%. On the other hand, the low-cost carbon-SiO₂ (C-SiO₂) hybrids prepared by furfuryl alcohol polymerization and pyrolysis were stable only for 15h; after that, the carbon of the hybrids decomposes completely rendering the almost inactive and non-selective silica matrix.
In this work we propose a strategy to enhance the thermal stability of these C/SiO$_2$ hybrids for the ODH reaction. It is well-known that phosphorous has an inhibiting effect on the carbon combustion [46-50]; in this study we investigated the effect of the P addition (on two loadings) on a furfuryl alcohol based silica hybrid. The performance of these P-modified hybrid catalytic materials is compared to state-of-the-art P/SiO$_2$ and MWCNT. The catalyst stability under the ODH reaction conditions will be evaluated from the combustion apparent activation energies.

4.2 Experimental methods

4.2.1 Materials

Bare precipitated amorphous silica extrudates (61138, denoted here as AS) was kindly supplied by Saint-Gobain NorPro, a Division of Saint-Gobain Ceramic Materials GmbH. Low SiO$_2$ stabilized $\gamma$-Al$_2$O$_3$ extrudates were kindly provided by Albemarle Catalysts B.V. Purified MWCNT (C>96 wt.% experimentally determined) was kindly supplied by Hyperion (CS-02C-063-XD). Activated carbons (denoted as AC) were supplied by Norit (ROX 0.8). For the impregnations, we employed the liquid pore volume ($V_{LPV}$) that was experimentally determined ($V_{LPV}$=1.05 cm$^3$.g$^{-1}$): water was added to ca. 10 g material that is repeatedly shaken after each water addition until the material turned shiny. Note that this method is different to the reported one by Innes [51] based on the caking of the catalyst particles that agrees with the gas adsorption pore volume. Note that $V_{LPV}$ (1.05 cm$^3$.g$^{-1}$) is larger than that of the gas adsorption value (0.842 cm$^3$.g$^{-1}$, AS in Table 1) because water fills pores larger than 100 nm. A similar $V_{LPV}$ was used for the (Furfuryl Alcohol) FA/SiO$_2$ composites during the P addition.

4.2.2.1 Catalyst preparation

4.2.2.1 Synthesis of the C/SiO$_2$ catalysts

Among the various carbon sources, we considered using the furfuryl alcohol polymerization [52-61] route since it has given successful examples of stable carbon nanoreplicas [62-64]. Commercial amorphous precipitated SiO$_2$ (AS) was used as support. The solid was pre-sieved into the 212-425 μm fraction that was obtained by crushing the commercial extrudates. The carbon precursor was added by incipient wetness impregnation of the carbon precursor using 5% extra liquid volume regarding the solid pore volume. Furfurylalcohol (FA, Acros Organics, 98%) was used as carbon precursor and oxalic acid (OA, Acros Organics, >99%) as catalyst.

The support (typically 3 g) was first degassed under vacuum at 150 °C during 4 h. A carbon-precursor solution was prepared by mixing FA and OA in a molar ratio of 250 based on previous polymerization studies [64] and water. Then 3.15 mL of the FA/OA aqueous solution was added to the support to obtain a carbon loading of 15 wt.%, in the final pyrolyzed hybrids; assuming that only carbon is present in the final composite material. The wet material was shaken (VWR, digital DVX-2500) during 4 minutes at 2500 rpm at room temperature to distribute the solution evenly. Afterwards, the FA polymerization of the samples was induced at 160 °C in an atmospheric oven during 8 h; the sample is named 15C/AS.
4.2.2.2 Preparation of the P/C/SiO$_2$ hybrid catalysts

The phosphorus was added onto the dried 15C/AS material before pyrolysis as diluted orthophosphoric acid ($\text{H}_3\text{PO}_4$); a solution (10 mL) was prepared by mixing
0.651 mL (or 1.345 mL) of $\text{H}_3\text{PO}_4$ (Merck, 85%) with water; then 3.15 mL of the
solution was (incipient wetness) impregnated into the 15C/AS dried material (3 g).
This corresponds to a phosphorous loading of ca. 3 or 6 wt.% (as P). Afterwards, the
samples were shaken during 4 min at 2500 rpm at room temperature and dried at
70 °C overnight in an atmospheric oven. The catalysts are denoted as 3P/15C/AS
and 6P/15C/AS.

4.2.2.3 Carbonization protocol

The carbonization of the C/SiO$_2$ and P/C/SiO$_2$ samples was carried out by pyrolysis in
a quartz-tube housed tubular oven (Nabertherm RT 50/250-11). The sample (~3 gram)
was loaded in a flat quartz crucible and placed horizontally in the centre of the
heating zone of the furnace. After closing and purging the tube for 30 min with $\text{N}_2$,
the sample was heated at 1 °C.min$^{-1}$ from room temperature until 700 °C for 3 h and
subsequent cooling down all in a nitrogen flow (150 mL.min$^{-1}$ NTP).

4.2.2.4 Preparation of the P/SiO$_2$ reference catalysts

Reference catalysts based on P on silica (3 and 6 wt.%) were prepared for comparison. The P addition protocol is nearly identical to that described above for the P/C/SiO$_2$ hybrid; using 212-425 μm pre-sieved AS material that was obtained by crushing the commercial extrudates. The samples were then shaken during 4 min at 2500 rpm at room temperature and dried at 70 °C overnight in an atmospheric oven. The samples were calcined in an air box furnace (Nabertherm LT9/11) from room temperature at 4 °C.min$^{-1}$ until at 500 °C and kept for 8 h. The catalysts are denoted as 3P/AS and 6P/AS.

4.2.3 Characterization

The total organic content of the fresh and spent catalysts was quantified by thermogravimetric analysis (TGA) on a Mettler-Toledo analyzer (TGA/SDTA851e) using a flow of synthetic air of 100 mL.min$^{-1}$ NTP. The temperature was increased from 30 to 900 °C at 10 °C.min$^{-1}$. Blank curve subtraction using an empty crucible was taken into account. The oxidation rate patterns (TPO) were obtained in the same instrument using the derivative of the TGA patterns. Elemental carbon, hydrogen, and nitrogen in the hybrids were analysed in a EuroVector 3000 CHNS analyser, after dissolving the silica and the complete removal of “PO$_x$” (40 wt.% HF, 2 days, at ambient temperatures). Approximately 2 mg of the organic derived material was accurately weighed in a 6-digit analytic balance (Mettler Toledo). The samples were completely (no ash deposits after the TGA experiment) burnt at 1800 °C in the presence of an oxidation catalyst and decomposed into CO$_2$, H$_2$O, and N$_2$. These gases were then separated in a Porapak QS column at 80 °C and quantified with a TCD detector. Acetonitrile (99.9 % purity) was used as an external standard. Oxygen content was calculated by difference.

Nitrogen physisorption analyses (~196 °C) were carried out in a Micromeritics ASAP 2020. The samples were degassed in vacuum at 250 °C for 10 h. The surface area was calculated using the standard BET method ($S_{\text{BET}}$) [65]. The single point gas adsorption (or internal) pore volume ($V_T$), below 100 nm, was estimated from the amount of gas adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distributions (PSD) were obtained from the BJH method [66] using the
adsorption branch of the isotherms; the mean pore size ($\phi_{BJH}$) is given by the position of the PSD maximum, while the $t$-plot method [67] was employed to quantify the micropore volume ($V_M$) and area ($S_M$). It is noted that the samples do not show microporosity and this was excluded from the discussion.

The apparent activation energy (AAE) of the carbon combustion was calculated by Ozawa method [68] using a correlation between peak temperature for a given conversion and the heating rate $\phi$ for four thermal analysis derivative curves (TGA). The TGA curves were obtained on a Mettler-Toledo analyzer (TGA/SDTA851e) using a flow of synthetic air of 100 mL.min$^{-1}$ NTP. The temperature was increased from 30 to 900 °C with a heating rate of 1, 3, 5, 10 °C.min$^{-1}$. Blank curve subtraction using an empty crucible was taken into account. The apparent activation energy was calculated for 20 and 80% conversion levels.

4.2.4 Catalytic tests

The catalytic tests were carried out in a 6-flow micro reactor using a fixed volume of catalyst (0.8 ml, corresponding to 65 mm of bed length) in down-flow 4 mm quartz reactors. To assure that the catalyst bed is located in the isothermal zone of the furnace, the reactors were loaded with quartz wool, 10 cm glass pearls (0.5 mm diameter), the catalyst, 10 cm glass pearls (0.5 mm diameter), and a second quartz wool plug. The glass pearls have limited conversion; less than 3% EB conversion under all applied conditions. The reactor gas feed is a mixture that can consist of CO$_2$, N$_2$, and air that counts for a gas-flow rate of 36 mL (NTP).min$^{-1}$; the liquid EB feed flow rate is 1 g/h (3.54 ml (NTP).min$^{-1}$ vapor) that is evaporated upstream each reactor in a $\alpha$-Al$_2$O$_3$ column, resulting in a 1:9 molar ratio of ethylbenzene to gas (10 vol. % EB). This corresponds with operation at a GHSV of 3000 l/l/h. The total pressure was 1.2-1.3 10$^5$ Pa. The reactor exhaust gas was analyzed by gas chromatography using a combination of columns (0.3m Hayesep Q 80-100 mesh with back-flush, 25m × 0.53mm Porabond Q, 15 m×0.53mm molsieve 5A, and RTX-1 with 30m×0.53mm) with TCD and FID detectors. This configuration allows quantifying permanent gases such as CO$_2$, H$_2$, N$_2$, O$_2$, CO as well as hydrocarbons (methane, ethane, ethene, benzene, toluene, ethylbenzene, styrene, and heavy aromatics). The catalytic tests were carried out under practical conditions of 20 % excess O$_2$ with respect to the ODH reaction and a concentrated EB feed of 10%. If not stated otherwise, for all EB conversion data the oxygen conversion is complete. All physical characterizations for the spent catalysts were done after the complete testing cycle of 60 h. A more complete description of the testing protocol can be found elsewhere [69].

4.3 Results

4.3.1 Characterization of the fresh hybrid catalysts

The thermal stability and amount of organic material of the hybrids was determined by TGA (Fig. S-1). The hybrid carbon starts to burn in air at around 450 °C with a maximum rate at 575 °C for both hybrids. The organic content of the P-hybrids is 17.2 and 19.1 wt. %. The oxidation stability in air was compared to the MWCNTs and a P-free counterpart (15C/AS) using the oxidation rate profiles (TPO, Fig. 1). Most of the materials start to burn in air above 450 °C, but the maxima vary among the samples; the most stable are MWCNT with a maximum at 625 °C. The maxima of the P-promoted hybrids virtually coincide with the 15C/AS material, so P has apparently no effect on inhibiting the combustion of the deposited carbon. However, the
determination of the apparent activation energies will give a more thorough interpretation of the thermal stability, as it was shown in our previous study [45].

**Figure 1.** Oxidation rate patterns (TPO) in air (10 °C.min⁻¹) for MWCNT, 3P/15C/AS, 6P/15C/AS, 15C/AS, spent 3P/15C/AS and spent 6P/15C/AS. Conditions: synthetic air, 100 ml.min⁻¹, heating rate of 10 °C. min⁻¹. Typical sample amount ranged 5-8 mg.

**Figure 2.** Ozawa-derived apparent activation energies (AAE, kJ.mol⁻¹) for the combustion at 80% conversion.
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Figure 2 shows the apparent activation energies (AAE) as determined by the Ozawa method. A clear trend is seen where the P-based hybrids have an increased AAE of around 13% higher than that of the 15C/AS, and lower than that of MWCNT (24% higher than 15C/AS). Therefore, the AAE predict a better thermal stability attributed to the P effect.

High oxygen content of the deposited carbon has been one of the crucial compositional features for the selective and active sites for the reaction-produced active coke in the EB ODH reaction [22]. The elemental composition of both 3P/15C/AS and 6P/15C/AS hybrids was determined by CHN (Table S-1) and compared to reported values for ODH cokes (Fig. S-2) [22,70]. The O:C ratios (0.10-0.15 at.) lie within the typical reported limits for ODH coke. Therefore, it can be expected that the FA-based hybrids will be readily active/selective for the ODH reaction. Studies about FA-based carbons, reports low O:C ratios (0.02-0.12) [54,56,57,59]. Burket et al. [59] demonstrated that the O removal takes place during the collapse of the mesopores. Thus the high O:C ratio in the 3P/15C/AS and 6P/15C/AS can be then attributed to the stable mesopores (in both cases 96% of the total pore volumes are mesoporous) due to the presence of the mesoporous silica support underneath that prevents the carbon collapse.

Other important features are the porosity of the hybrid material in comparison to the fresh silica and the type of coke formed. The Raman spectra of both materials (3P/15C/AS and 6P/15C/AS, Fig. S-3) reveal two broad superimposing adsorptions centered at 1610 and 1375 cm$^{-1}$, which are characteristic of aromatic and amorphous carbon (G and D peaks, respectively) [71,72].

Comparison of the gas adsorption N$_2$ isotherms was done in Figure 3. The shape of the isotherms does not change upon deposition of carbon and phosphorous; isotherms of type IV with hysteresis HI were observed as for the bare AS silica; representing solids with cylindrical highly uniform pores [73,74]. No pore network effects were observed, indicating that the pores are well connected after the carbon/phosphorous addition. There is, however, a substantial reduction of the pore volume of 37% (3P/15C/AS) and 42% 6P/15C/AS); while the surface area only changes 8 and 18%, respectively. The t-plot analysis evidence the formation of micropores that contribute in 22-23% of the total surface area (Table S-2). Therefore, there are two opposing effects on the texture; significant reduction of mesopore volume and formation of micropore volume will overall result in a slight reduction of the total surface area. This happens because the created micropores contribute significantly to the surface area. The BJH pore size distribution in Figure 3 (inset) shows a decrease of the intensity, associated to the filling effect of the carbon. Calculation of the average geometrical pore size (Table 1) reveals a reduction of pore size from 15.8 nm (AS) to 10.9 nm (3P/15C/AS) and 11.3 nm (6P/15C/AS). Therefore, the overall interpretation of the textural data is that a P-containing carbon coating has been created with the shrinking of the existing mesopores and the formation of new micropores. Both will contribute in maintaining a relatively high surface area.
**Figure 3.** Nitrogen sorption isotherms at −196 °C for AS-700, 3P/15C/AS, and 6P/15C/AS. Inset: BJH pore size distribution.

**Table 1.** Textural parameters derived from N$_2$ adsorption at −196 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{BET} (m^2.g^{-1})$</th>
<th>$V_T (cm^3.g^{-1})$</th>
<th>$\phi_{BJH} (nm)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS bare</td>
<td>213</td>
<td>0.842</td>
<td>20.8 (15.8)</td>
</tr>
<tr>
<td>3P/15C/AS</td>
<td>195 (-8)$^b$</td>
<td>0.532 (-37)$^b$</td>
<td>22.1 (10.9)</td>
</tr>
<tr>
<td>3P/15C/AS spent</td>
<td>58 (-70)$^a$</td>
<td>0.128 (-76)$^a$</td>
<td>broad (8.8)</td>
</tr>
<tr>
<td>6P/15C/AS</td>
<td>174 (-18)$^b$</td>
<td>0.492 (-42)$^b$</td>
<td>23.3 (11.3)</td>
</tr>
<tr>
<td>6P/15C/AS spent</td>
<td>42 (-76)$^a$</td>
<td>0.101 (-79)$^a$</td>
<td>broad (9.6)</td>
</tr>
<tr>
<td>MWCNT</td>
<td>406</td>
<td>1.100</td>
<td>3, 30.8</td>
</tr>
<tr>
<td>3P/AS</td>
<td>165</td>
<td>0.765</td>
<td>21.9 (18.5)</td>
</tr>
<tr>
<td>3P/AS spent</td>
<td>61 (-63)$^a$</td>
<td>0.155 (-80)$^a$</td>
<td>22.5 (10.1)</td>
</tr>
<tr>
<td>6P/AS</td>
<td>74</td>
<td>0.682</td>
<td>140 (36.9)</td>
</tr>
<tr>
<td>6P/AS spent</td>
<td>56 (-24)$^a$</td>
<td>0.392 (-43)$^a$</td>
<td>broad (28.0)</td>
</tr>
<tr>
<td>AC</td>
<td>959</td>
<td>0.609</td>
<td>broad</td>
</tr>
</tbody>
</table>

$^a$ Value in parenthesis is the % of reduction with respect to the fresh material; $^b$ % of reduction with respect to the AS bare; $^c$ gas adsorption or internal pore volume; $^d$ values in parenthesis are the average geometrical pore size as 4.10*$V_T$/S$_{BET}$.

### 4.3.2 Pseudo-steady state EB ODH catalyst performance

The catalyst performances are summarized in Figure 4; EB conversion, selectivity to CO$_x$ selectivity to ST, and ST yield are represented as a function of time-on-stream (TOS) at various temperatures and O$_2$:EB ratios. The selectivities to side products (not shown) are small and almost constant as a function of the reaction conditions. Benzene/toluene are formed in low percent concentrations along with trace amounts of oxygenates, the selectivities to these byproducts do not substantially vary. The sum of ST and CO$_x$ selectivities (Fig. 4-b and -c) is on average above 96% of the converted ethylbenzene.
Figure 4 compares the P-hybrids with various types of relevant EB ODH catalysts under similar conditions. It was found that the P-hybrids are stable. Although there is a slight gasification/burning as reflected in the CO\textsubscript{x} profiles, the P-hybrids were stable for 60 h. In our previous work [45] we reported that the P-free hybrid (15C/AS), starts to decompose after 20 h with the complete disappearance of the introduced carbon and no conversion after 35 h on the bare silica. Therefore, the addition of P has a remarkable effect on the stability. This is consistent with the calculated apparent activation energies that showed values for the P-hybrids close to the MWCNT.

The performance of the P-hybrids is compared to state-of-the-art P/SiO\textsubscript{2}, MWCNT and prior work on C/SiO\textsubscript{2} hybrids. The selectivity to ST ranges 85-90%, which is high, but slightly lower when compared to the P/SiO\textsubscript{2} counterparts and much better than C/SiO\textsubscript{2} [46] that ranged between 50 and 80%. A more competitive carbon-based catalyst would be the MWCNT. When the ST selectivity or EB conversion of these P-based hybrids are compared to the MWCNT, it can be seen that the P-hybrids behave much better at high temperatures (450-475 °C) both, in conversion and selectivity, while the difference becomes negligible at lower temperature (425 °C). The trends in selectivity were opposing; while the selectivity of the MWCNT was best at lower temperature (in agreement with literature that often reports a range between 350-400 °C operation temperatures), higher temperature were most favourable for the P-hybrids. Thus, the P-hybrids seem to be a high-temperature catalyst for this application with higher selectivity and conversion than that of MWCNT.

An additional remarkable feature is that the P-hybrids are readily active/selective, while the P-based silica catalysts (3P/AS and 6P/AS) require substantial time to reach the pseudo-stationary conversion (Fig. 4-a); 8 and 15 h respectively, under the applied conditions. This is thought to be due to the slow formation of active coke on the catalyst surface, induced by the acidity of the phosphates groups [10,21]. This deposited coke is readily selective since the selectivity profiles do not have such activation period (Fig. 4-b). The ST yield of these P/silica catalysts (Fig. 4-d) is determined by a complex activation-deactivation phenomena of the conversion, related to the unlimited coke build up process.

When comparing the performance at 450 °C between the second and last sequence in the catalytic test, it can be observed that the P-based hybrids drop in conversion; the conversion levels do not come back to the values recorded in the second cycle but decline. This can be associated to the on-going coking, though other deactivating phenomena associated to the silica itself cannot be ruled out. Despite this, it is noteworthy that such a drop is much lower than those for MWCNT and P/SiO\textsubscript{2} catalysts.
In conclusion, the P-based hybrids show remarkable features. They lack of the stabilization period, i.e. readily active/selective, and the selectivity and conversion at high temperature (450-475 °C) are superior when compared to the MWCNT. The difference in selectivity and conversion becomes negligible when working at 425 °C. They seem to be thermally stable, with no apparent gasification/burning for 60 h under the applied harsh reaction conditions; the on-going deactivation is less extensive than the other reference catalysts tested.

4.3.3 Spent catalysts and deactivation

The coke content in the spent catalysts was determined by TGA (Fig. S-4) and the coke build-up was calculated by the difference with the starting organic loading. Figure 5 shows that the P-hybrids build up coke during the reaction to ca. 23 wt. %. Thus, P can stabilize the FA-based coating but apparently also builds up additional coke. The P/AS samples also build coke in a much wider range, from 14% (6P/AS) to 43% (3P/AS), which is related to the differences in the surface areas of the fresh catalysts. It is not strictly proportional, but also to the fact the 6P/AS is still in the activation process, so not all the surface has been covered by coke.
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Figure 5. Organic contents for the fresh and spent catalysts after reaction. Coke build-up is defined as the difference (spent – fresh). Raw data are given in Table S-5 and TGA patterns in Fig. S-4.

Chemical analysis proves higher oxygen content of the spent hybrid catalysts than that of the fresh counterparts (Table S-1); it comes from the additional coke formed during the reaction. The higher O content is consistent with a more facile oxidation in air, evidenced by a shift towards lower temperatures in the TGA maxima (Fig. 1). Representation of the composition in a modified van Krevelen plot (Fig. S-2) shows significant changes. The C:H varies from a relatively high ratio, characteristic of FA-based carbons having low H content [54,56,57,59], to lower ratios, near the values often reported for the ODH coke (Fig. S-2). It is obvious, that the fresh hybrid catalysts can not be hydrogenated under the ODH conditions. Hence this compositional effect is ascribed to the deposition of new ODH coke that is richer in H during the reaction.

Raman spectra of the spent hybrid catalysts indicate the presence of a more ordered structure that has been formed during the reaction. The D/G peak ratio becomes smaller (Fig. S-3 and Table S-6) and this can be explained by two effects: 1) removal of the more amorphous carbon domains by gasification/burning and 2) deposition of sp$^2$-rich carbon materials, or 3) both effects. The latter is due to the buildup of new polyaromatic ODH coke.

Therefore, TGA/TPO, CHN, and Raman reveal the formation of a coke with different nature than the starting hybrid.

The porosity of the spent hybrids evidences that reduction of surface area and pore blockage is the main source of catalyst modification during the applied testing protocol. The specific surface area and pore volume are reduced around 70-80% for both parameters (Table 1) resulting in a less active catalytic system. The isotherms change the shape having a closure point around 0.45 in the relative pressure (Fig. S-5) indicating the presence of pore network restrictions associated to the overcoking from the reaction. The spent 3P/AS and 6P/AS also manifested a substantial reduction of surface area (63 and 24%) and pore volume (80 and 43%) (Table 1, Fig. S-6). The 3P/AS has pore network effects, while 6P/AS does not because it has much larger pores. The 6P/AS is less affected possibly because the surface is not yet fully covered in coke. The conversion keeps increasing after 55 h which is an indication of on-going coke build-up.

Thus, overcoking is identified as responsible for the decrease of texture for both, P/silica and P/C/silica hybrids during reaction.
4.4 Conclusions

A composite material based on the polymerization and pyrolysis of furfuryl alcohol on a commercial silica, containing P is stable under relevant EB ODH conditions up to 60 h TOS. This composite material was readily active and highly selective. It is shown that P has a combustion inhibiting effect as well as it contributes to the selectivity greatly. The P-hybrid materials outperform at high temperatures (450-475 °C) the hybrid catalysts, while the differences with respect to MWCNT become negligible at lower temperature (425 °C), with a lower conversion. Both, conversion and selectivity were optimal at high temperature, which makes this hybrid a better alternative than MWCNT. Overcoking with a reduction of pore volume and surface area takes place during the reaction, while the composition of the carbon gets richer in O due to the deposited coke. The apparent activation energies predicted the thermal stability under the ODH reaction conditions.

4.5 References

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Appendix Chapter 4
Figure S-1. TGA patterns of the fresh hybrids: 3P/15C/AS and 6P/15C/AS. Conditions: 100 ml.min⁻¹, synthetic air, heating rate of 10 °C.min⁻¹.

Table S-1. Chemical composition of the organic material after dissolution of the silica matrix and "PO₄"-removal by HF treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt.%)</th>
<th>H (wt.%)</th>
<th>O (wt.%)</th>
<th>Compositional formula (at.)</th>
<th>C:H (at.)</th>
<th>O:C (at.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3P/15C/AS</td>
<td>83.1</td>
<td>1.6</td>
<td>15.3</td>
<td>C_{7.23}H_{1.62}O</td>
<td>4.57</td>
<td>0.14</td>
</tr>
<tr>
<td>3P/15C/AS spent</td>
<td>78.6</td>
<td>2.1</td>
<td>19.4</td>
<td>C_{5.39}H_{1.68}O</td>
<td>3.22</td>
<td>0.19</td>
</tr>
<tr>
<td>6P/15C/AS</td>
<td>79.9</td>
<td>1.4</td>
<td>18.6</td>
<td>C_{5.73}H_{1.21}O</td>
<td>4.73</td>
<td>0.17</td>
</tr>
<tr>
<td>6P/15C/AS spent</td>
<td>77.6</td>
<td>2.1</td>
<td>20.3</td>
<td>C_{5.10}H_{1.63}O</td>
<td>3.13</td>
<td>0.20</td>
</tr>
</tbody>
</table>
**Figure S-2.** Modified Van Krevelen plots representing the composition of the hybrids (○): (3P/15C/AS and 6P/15C/AS), fresh and spent, in comparison with prior work, adapted from [●,70] and [■,22]. Raw data are given in Table S-1.

**Figure S-3.** Raman spectra for the fresh and spent 3P/15C/AS and 6P/15C/AS catalysts.
Table S-2. Micropore area and volume derived from the t-plot method from N₂ adsorption volumetric data at −196 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>( S_m ) (m²·g⁻¹) (^a)</th>
<th>( V_m ) (cm³·g⁻¹) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS bare</td>
<td>BD c</td>
<td>BD c</td>
</tr>
<tr>
<td>AS-700</td>
<td>BD c</td>
<td>BD c</td>
</tr>
<tr>
<td>AS-900</td>
<td>BD c</td>
<td>BD c</td>
</tr>
<tr>
<td>AS-1100</td>
<td>BD c</td>
<td>BD c</td>
</tr>
<tr>
<td>3P/AS</td>
<td>10 (165)</td>
<td>0.003 (0.765)</td>
</tr>
<tr>
<td>3P/AS spent</td>
<td>5 (61)</td>
<td>0.002 (0.155)</td>
</tr>
<tr>
<td>6P/AS</td>
<td>2 (74)</td>
<td>&lt;0.001 (0.682)</td>
</tr>
<tr>
<td>6P/AS spent</td>
<td>5 (56)</td>
<td>0.002 (0.392)</td>
</tr>
<tr>
<td>3P/15C/AS</td>
<td>43 (195)</td>
<td>0.020 (0.532)</td>
</tr>
<tr>
<td>3P/15C/AS spent</td>
<td>6 (58)</td>
<td>0.002 (0.128)</td>
</tr>
<tr>
<td>6P/15C/AS</td>
<td>40 (174)</td>
<td>0.019 (0.492)</td>
</tr>
<tr>
<td>6P/15C/AS spent</td>
<td>3 (42)</td>
<td>0.001 (0.101)</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>BD c</td>
<td>BD c</td>
</tr>
<tr>
<td>( \gamma )-Al₂O₃</td>
<td>BD c</td>
<td>BD c</td>
</tr>
</tbody>
</table>

\( ^a \) Values in parenthesis are the total BET surface area and \( ^b \) total pore volume.

\( ^c \) BD: the micropore area is not reported because either the micropore volume is negative or below the detection limit (<0.001 cm³·g⁻¹).

Table S-3. The apparent activation energies of the combustion of fresh catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( E_a ) at 80% conversion, kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>15C/AS</td>
<td>116</td>
</tr>
<tr>
<td>3P/15C/AS</td>
<td>131</td>
</tr>
<tr>
<td>6P/15C/AS</td>
<td>129</td>
</tr>
<tr>
<td>MWCNT</td>
<td>144</td>
</tr>
</tbody>
</table>
Phosphorous-induced thermal stabilization for carbon-supported SiO$_2$ catalysts in the oxidative dehydrogenation of ethylbenzene to styrene.

**Figure S-4.** TGA patterns of the spent catalysts: a) 3P/15C/AS; b) 6P/15C/AS; c) 3P/AS, and d) 6P/AS. Conditions: 100 ml.min$^{-1}$, synthetic air, heating rate of 10 °C.min$^{-1}$.

**Table S-5.** TGA weight loss at 200-900 °C from the patterns of the spent catalysts from Fig. S-4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA weight loss 200-900 °C (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3P/15C/AS</td>
<td>42.8</td>
</tr>
<tr>
<td>6P/15C/AS</td>
<td>40.5</td>
</tr>
<tr>
<td>3P/AS</td>
<td>42.9</td>
</tr>
<tr>
<td>6P/AS</td>
<td>13.7</td>
</tr>
</tbody>
</table>

**Table S-6.** Raman characterization of the fresh and spent catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3P/15C/AS</td>
<td>1.58</td>
</tr>
<tr>
<td>3P/15C/AS spent</td>
<td>0.99 (-37%, respect to fresh)</td>
</tr>
<tr>
<td>6P/15C/AS</td>
<td>1.62</td>
</tr>
<tr>
<td>6P/15C/AS spent</td>
<td>1.18 (-27%, respect to fresh)</td>
</tr>
</tbody>
</table>
Figure S-5. **Top**) Nitrogen sorption isotherms at −196 °C of the spent and fresh catalysts 3P/15C/AS and 6P/15C/AS. Inset: BJH pore size distribution. **Bottom**) Zoom-in of the spent catalysts’ isotherms. The arrow indicates the low-pressure closure point at ca. 0.45 p/p₀ in the desorption step. Solid line: adsorption step; dashed line: desorption step.
Phosphorous-induced thermal stabilization for carbon-supported SiO\textsubscript{2} catalysts in the oxidative dehydrogenation of ethylbenzene to styrene.

**Figure S-6. Top**) Nitrogen sorption isotherms at –196 °C of the spent and fresh catalysts 3P/AS and 6P/AS. Inset: BJH pore size distribution. **Bottom**) Zoom-in of the spent catalysts’ isotherms. The arrow indicates the low-pressure closure point at ca. 0.45 \( p/p_0 \) in the desorption step. Solid line: adsorption step; dashed line: desorption step.