Chapter 3

On the stability of conventional and nanostructured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions

Relevant carbon-based materials, home-made carbon-silica hybrids, commercial activated carbon, and nanostructured multi-walled carbon nanotubes (MWCNT) were tested in the oxidative dehydrogenation of ethylbenzene (EB). Special attention was given to the reaction conditions, using a relatively concentrated EB feed (10 vol. % EB), and limited excess of O₂ (O₂:EB=0.6) in order to work at full oxygen conversion and consequently avoid O₂ in the downstream processing and recycle streams. The temperature was varied between 425-475 °C, that is about 150-200 °C lower than that of the commercial steam dehydrogenation process. The stability was evaluated from runs of 60 h time on stream. Under the applied reactions conditions, all the carbon-based materials are apparently stable in the first 15 h time on stream. The effect of the gasification/burning was significantly visible only after this period where most of them fully decompose. The carbon of the hybrids decomposes completely rendering the silica matrix and the activated carbon bed is fully consumed. Nano structured MWCNT is the most stable; the structure resists the demanding reaction conditions showing an EB conversion of ~30% (but deactivating) with a steady selectivity of ~80%. The catalyst stability under the ODH reaction conditions is predicted from the combustion apparent activation energies.
3.1 Introduction

Styrene (ST) is one of the major platform chemicals. It is the monomer for polystyrene formulations and an essential additive for tires, and many more small-scale uses. The global production of styrene in 2010 was 25 million metric tons and it is forecast to grow at an average of 3.6% per year [1]. It is industrially produced for about 85% by steam dehydrogenation (also called direct dehydrogenation) of ethylbenzene (EB) in an excess of steam over a K-promoted Fe₂O₃ catalyst [2,3], eq. 1.

\[
\text{EB} \rightleftharpoons \text{ST} + \text{H}_2
\]  

The catalyst is highly selective to styrene, typically >97%, and stable [2]. One of the aspects for improvement is reducing the huge amount of steam needed to carry out the dehydrogenation chemistry, which is an endothermic process. Thermodynamic limitation of direct dehydrogenation is also a reason why new routes for the styrene production are still investigated. The use of oxidants, such as O₂ [4, 5], is very promising because the reaction is shifted by producing H₂O, eq. 2. The equilibrium dehydrogenation boundary is broken (with O₂) and this allows operating at lower temperature as long as an active, selective, and stable catalyst is available.

\[
\text{EB} + \frac{1}{2} \text{O}_2 \rightarrow \text{ST} + \text{H}_2\text{O}
\]

This oxidative pathway was initially studied over inorganic supports, such as alumina [6]. It was demonstrated that the coke deposited on the oxide’s surface having acid Lewis sites, generated during the early stage of the reaction is the actual “coke” catalyst [6-9]; this is supported by a recent study [10]. The coke was characterized as polyaromatic having a relatively high oxygen content (O:C=0.10-0.15 at.); the proposed active sites are surface ketonic groups that act as redox sites for hydrogen abstraction from EB [11-14].

Carbon based materials have been investigated broadly on this reaction, trying to reduce or eliminate the ‘activation period’ (i.e. formation of the active/selective carbonaceous species) that occurs over the oxides. Activated carbons [15-29], carbon nanofibers [30-37], onion-like carbons [38-40], diamonds [26,28,40], nanofilaments [30], graphites [17,28,30,34], multiwall carbon nanotubes (MWCNTs) [26,28,36,39-49], and other type of carbon materials or mixtures of the above mentioned [50-54] have been studied for this reaction. It is generally found that these materials are readily active and selective; the reported selectivities are moderate lying between 55-85%. In some cases the reported selectivity is exceptionally high, in the range of 90-97% [28,46,47]. Under the reported reaction conditions and time frame most of the carbon-based materials are stable with the exception of the activated carbons that are steadily decomposed [20,21,26,43]; the rate of gasification/burning is faster than that of the coke buildup. Some of the most stable systems are the carbon nanotubes and ordered mesoporous carbons, though they show a pronounced initial deactivation in 5 h; from 35 to 20 mmol.g⁻¹h⁻¹[26] while Su et al. reported a decay from 90 to 70% EB conversion in a time frame of 5 h as well [51]. A similar initial deactivation was observed for furfuryl alcohol-based CMK-3 type carbons [54].

Comparing the reaction performance and catalyst stability among the reported studies is difficult, as the reaction conditions vary enormously. In addition to that, the used EB concentration is mostly relatively low, ranging 2-4 vol. % and the O₂:EB ratio is far above the stoichiometric, 1-5. From a practical stand point, it is desirable to operate at higher EB concentration, for higher product yield, and at complete O₂ conversion. The latter aspect is very important when looking at the overall process in order to avoid O₂ in the downstream processing and recycle streams. The thermal
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Stability is typically studied at low reaction temperatures, where the rate of gasification and combustion are limited, and likely not seen in the reported cycle. It should be noted that for a catalytic fixed bed operation a temperature rise of more than 100 °C will occur with only 25 % EB conversion with 100 % selectivity towards ST. Hence, it is essential to evaluate the catalyst stability at higher temperatures.

The objective of this study is to investigate the catalytic performance and stability of various types of carbon-based materials (tailor made with controlled carbon loading, nature and commercial ones) in the oxidative dehydrogenation of EB under identical and industrially relevant conditions; using a concentrated EB feed of 10 vol.%, a limited excess of O₂ (20 % excess O₂, equivalent to O₂:EB=0.6) in order to have full oxygen conversion. The proposed temperature range is between 425-475 °C, which is nearly 150-200 °C lower than that of the conventional steam dehydrogenation process. The high initial reaction temperature at 475 °C intends to assess the gasification and combustion under demanding conditions to see changes in a reasonable time frame (<60 h). However, this range also mimics what would happen if the reactor suffers an undesired temperature increase due to a moderate hot-spot (typically carbons are evaluated in EB ODH at 400-425 °C) or a moderate adiabatic temperature increase over a fixed catalyst bed reactor operation. Physico-chemical characterization of the fresh and spent catalysts was carried out to understand the catalyst life behaviour; the apparent activation energies of the combustion were particularly useful to rationalize the results.

3.2 Experimental

3.2.1 Materials

Commercial amorphous SiO₂ (denoted as AS, entry 1 in Table 1) used for the hybrid catalysts preparation was supplied by Saint-Gobain NorPro (SS61138). Activated carbons (AC, entry 2 in Table 1) were supplied by Norit (ROX 0.8), and purified MWCNT (C>96 wt.%) was obtained from Hyperion (CS-02C-063-XD). All materials were supplied in pellets, which were crushed and sieved in the fraction 212-425 µm. Furfurylalcohol (Acros Organics, 98%), D(+)-glucose (anhydrous for biochemistry, Merck 1.08337.1000), H2SO4 (1.00731.1000, Merck, 95-97% for analysis), and oxalic acid (Acros Organics, >99%) were employed without further purification for the preparation of the carbon-silica hybrids.
Table 1. Summary of sample codes and their preparative conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample code</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AS</td>
<td>Commercial amorphous silica, Saint-Gobain Norpro SS61138.</td>
</tr>
<tr>
<td>2</td>
<td>AC</td>
<td>Commercial activated carbon, Norit ROX 0.8.</td>
</tr>
<tr>
<td>3</td>
<td>MWCNT</td>
<td>Commercial multi-walled carbon nanotubes, Hyperion CS-02C-063-XD.</td>
</tr>
<tr>
<td>4</td>
<td>AS-700</td>
<td>AS material calcined at 700 °C.</td>
</tr>
<tr>
<td>5</td>
<td>AS-900</td>
<td>AS material calcined at 900 °C.</td>
</tr>
<tr>
<td>6</td>
<td>AS-1100</td>
<td>AS material calcined at 1100 °C.</td>
</tr>
<tr>
<td>7</td>
<td>G/AS700</td>
<td>Polymerization of glucose and pyrolysis at 700 °C over AS support.</td>
</tr>
<tr>
<td>8</td>
<td>G/AS900</td>
<td>Polymerization of glucose and pyrolysis at 900 °C over AS support.</td>
</tr>
<tr>
<td>9</td>
<td>FA/AS700</td>
<td>Polycondensation of furfuryl alcohol and pyrolysis at 700 °C over AS support.</td>
</tr>
<tr>
<td>10</td>
<td>FA/AS900</td>
<td>Polycondensation of furfuryl alcohol and pyrolysis at 900 °C over AS support.</td>
</tr>
<tr>
<td>11</td>
<td>FA/AS1100</td>
<td>Polycondensation of furfuryl alcohol and pyrolysis at 1100 °C over AS support.</td>
</tr>
</tbody>
</table>

For the impregnations, the liquid pore volume ($V_{LPV}$) of the bare silica was used [55], which was experimentally determined ($V_{LPV}=1.05 \text{ cm}^3\text{.g}^{-1}$) as follows: water was added to ca. 10 g material that is repeatedly shaken after each water addition until the material turned shiny. The $V_{LPV}$ ($1.05 \text{ cm}^3\text{.g}^{-1}$) is larger than the gas adsorption $V_T$ value (0.842 cm$^3\text{.g}^{-1}$, AS in Table 2) because water fills pores larger than 100 nm, which is the upper limit in gas adsorption.

Table 2. Textural parameters of the AS modified materials derived from N$_2$ adsorption at −196 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{BET} \text{ (m}^2\text{.g}^{-1})$</th>
<th>$V_T \text{ (cm}^3\text{.g}^{-1})$</th>
<th>$\Phi_{BJH} \text{ (nm)}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>213</td>
<td>0.842</td>
<td>20.8 (15.8)</td>
</tr>
<tr>
<td>AS-700</td>
<td>220</td>
<td>0.879</td>
<td>20.8 (15.9)</td>
</tr>
<tr>
<td>AS-900</td>
<td>110</td>
<td>0.388</td>
<td>17.8 (14.1)</td>
</tr>
<tr>
<td>AS-1100</td>
<td>&lt;2</td>
<td>0.002</td>
<td>broad</td>
</tr>
</tbody>
</table>

*a. Values in parenthesis are the average geometrical pore size calculated by $4.10^3V_T/S_{BET}$. |

3.2.2 Thermal stability of the amorphous silica support

The thermal stability of the AS support was investigated by analysing the textural and structural properties of the material that was subjected to heat treatment at 700, 900, and 1100 °C under dried nitrogen. These treatments were carried out in LT9/11 Nabertherm box furnace. The obtained samples correspond to entries 4-6 in Table 1.

3.2.3 Preparation of hybrid-silica hybrids

3.2.3.1 Furfuryl alcohol based SiO$_2$ hybrid materials

The carbon was added by incipient wetness impregnation of the carbon precursor using 5% extra liquid volume regarding the liquid pore volume, $V_{LPV}$. Furfurylalcohol
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(FA) was used as carbon source and oxalic acid (OA) as polymerization catalyst. Three grams of support was degassed under vacuum at 150 °C during 4 h. An aqueous solution containing the carbon precursor was prepared by mixing FA and OA in a molar ratio of 250 based on previous studies [56]. 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 material, assuming that only carbon is present in the final material. The wet material was shaken (VWR, digital DVX-2500) during 4 min at 2500 rpm at room temperature to distribute the solution evenly. Afterwards, the FA polymerization was induced by heating the sample at 160 °C in an atmospheric oven during 8 h. The samples prepared under this protocol are summarized in Table 1, entries 9-11.

3.2.3.2 Glucose based carbon-SiO$_2$ hybrids

Glucose (G) was also investigated as carbon source and H$_2$SO$_4$ as a catalyst in molar ratio of G/H$_2$SO$_4$=0.5 [57] for the hybrid catalysts preparation. The protocol is identical to above mentioned for FA, using a similar carbon loading in the final hybrid, ca. 15 wt.%. The samples prepared under this protocol are summarized in Table 1, entries 7 and 8.

3.2.4 Carbonization

The carbonization of the organic precursor was carried out by pyrolysis in a quartz-tube housed tubular oven (Nabertherm RT 50/250-11). The sample was loaded in a flat quartz crucible that was placed horizontally in the centre of the furnace heating zone. After closing and purging the tube for 30 min with a flow of dry N$_2$ (150 mL.min$^{-1}$ NTP), the sample was heated at 1 °C.min$^{-1}$ from room temperature until 700, 900, 1100 °C and kept for 3 h; the sample was kept under N$_2$ flow during the cooling down until room temperature.

3.2.5 Catalysts characterization

The 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$^{-1}$ STP. 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. Nitrogen physisorption analyses (−196.2 °C) were carried out in a Micromeritics ASAP 2020. The samples were degassed in vacuum at 200 °C for 10 h. The surface area was calculated using the standard BET method ($S_{BET}$) [58]. The single point gas adsorption pore volume ($V_T$) was calculated 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 [59] using the adsorption branch of the isotherms. The mean pore size ($\phi_{BJH}$) is given by the position of the PSD maximum. The t-plot method [60] was employed to quantify the micropore volume ($V_m$).

High resolution transmission electron microscopy (HR-TEM) images were acquired using a TEM/STEM JEOL 2100F operated at 200 kV. Samples were prepared by grinding, dispersion in ethanol and evaporative deposition onto holey carbon films on 300 mesh Cu grids.
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Powder X-ray diffraction (XRD) measurements were done on a Bruker D8 powder X-ray diffractometer using CuKα radiation, λ=0.154056 nm. The spectra were recorded with a step size of 0.02° and 3 seconds of accumulation time, in the 2θ angle range of 10-60°.

Raman spectra were obtained with 785 nm excitation line, 30 mW on the Perkin Elmer Ramanstation 400 spectrometer.

The apparent activation energy of the carbon combustion was calculated by Ozawa method [61] using a correlation between peak temperature for a given conversion and the heating rate ϕ for four thermal analysis derivative curves (DTA). The DTA 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.

3.2.6 Catalyst performance protocol

The catalytic tests were done in a 6-flow micro reactor using a fixed volume of catalyst (0.8 mL, corresponding to 65 mm of bed length) in 4 mm quartz reactors in down-flow mode. To guarantee 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 beads have limited conversion; less than 3% EB conversion under all applied conditions. The reactor gas feed is a mixture that can consist of CO₂, N₂, 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⁻¹ (3.54 mL STP.min⁻¹ vapor) that is evaporated upstream each reactor in a α-Al₂O₃ 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 1.2-1.3·10⁵ 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) and TCD and FID detectors. This configuration allows quantifying permanent gases such as CO₂, H₂, N₂, O₂, CO as well as hydrocarbons (methane, ethane, ethene, benzene, toluene, ethylbenzene, styrene, and heavy aromatics). The catalytic test was carried out at various temperatures (475, 450, 425, and 450 °C) and O₂/EB = 0.6 and 0.2 (vol.) to access the effect of temperature and O₂:EB on conversion and selectivity. It is noted that for low EB conversion (<15%) there was a considerable error in the ST/COₓ selectivities leading to substantial noise. For the sake of clarity, some graphs are, therefore, plotted until 30 h TOS. For all EB conversion data the oxygen conversion is 100%, unless otherwise is stated. All physical characterizations for the spent catalysts were done after the complete testing cycle of 60 h. The applied temperature program, starting at 475 °C for 15 h, was chosen to accelerate the gasification/combustion processes under the applied reaction conditions.

3.3 Results and discussion

3.3.1 Thermal stability of the bare silica support

The support used in this study is commercial precipitated silica, whose thermal stability was studied by gas adsorption and XRD analysis of the thermally treated materials between 700-1100 °C. Characterization by gas adsorption of the bare silica shows well-defined mesopores centered at 19.1 nm (AS in Fig. 1). The isotherm is type IV with hysteresis H1 [62,63]; representing solids with cylindrical pore
geometry with relatively high pore size uniformity and facile pore connectivity. This is consistent with the TEM micrographs that show pores defined by the interspace of nanoparticles ranging 5-30 nm (Fig. 2). The average particle size was calculated assuming the particles to be spherical using the $S_{\text{BET}}$ and the skeletal density for the silica ($2.3 \times 10^3$ kg.m$^{-3}$, experimentally determined by helium picnometry). The particle size was found to be around 12 nm on average which is consistent with TEM micrographs (Fig. 2-b). XRD analysis evidences that the bare AS silica is structurally formed by amorphous particles (AS in Fig. 3).

![Figure 1.](image-url) Nitrogen sorption isotherms at –196 °C for the bare amorphous silica (AS) and calcined AS-700, AS-900 and AS-1100. Inset: BJH pore size distributions.
Figure 2. a) TEM micrograph and b) HR-TEM micrograph of the bare silica support indicating the dimension of some particles. Scale bar = 20 nm

Figure 3. Powder XRD patterns: bare silica, AS-700, AS-900, and AS-1100. Phase identification: C (cristobalite) and T (tridymite) [64].

At 700 °C the silica remains almost unchanged; the XRD reflection at 22° is still broad (AS-700 in Fig. 3) and the N₂ isotherm is almost identical to the fresh AS material (Fig. 1). Consequently the surface area, pore volume, and pore size remains almost identical (Table 2), with differences in the physical values within 5% higher values. The higher values are attributed to the cleaning of the sample surface upon thermal treatment. When the temperature is increased to 900 °C, the material suffers from a sintering process. Although the XRD reflection is rather similar (AS-
900 in Fig. 3), the material adsorbs significantly less \( \text{N}_2 \) gas (Fig. 1); the surface area and pore volume are reduced to ca. half of the initial values (Table 2). The pore size is also diminished with the pore maxima shifted to 17.8 nm while the average geometrical pore size is reduced with 11%. These are all indications for thermal sintering. Severe changes occurred at 1100 °C, where the amorphous silica is transformed into a mixture of cristobalite and tridymite polymorphs [64] (AS-1100 in Fig. 3) and both those transformations have almost no surface area nor pore volume (Table 2).

The textural properties of thermally treated silicas were compared to the furfuryl alcohol-silica hybrids that after impregnating the carbon source, and acid catalyzed polymerization, were pyrolyzed between 700-1100 °C; denoted as FA/AS700, FA/AS900 and FA/AS1100 (see Table 1). The textural comparison can be found in Figure 4. The three hybrids show typical isotherms for a micro- and mesoporous material, type IV with hysteresis H1. Comparison of the isotherms for FA/AS700 and the AS-700 counterpart (Fig. 4-a) points out that the hybrid adsorbs more gas in the low range of the isotherm (0-0.3 p/p\(_o\)), and, consequently, it has a higher surface area (cf. values reported in Table 2 and 3). This is attributed to the enhanced micropore volume, that is near 3 times higher than that of the silica AS-700 (cf. values given in Table S-1 for AS-700 and FA/AS700), while the total pore volume of the hybrid is inferior (Table 3).

Table 3. Summary of characterization data derived from \( \text{N}_2 \) physisorption, TGA, and Raman for the fresh and spent catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) m(^2)g(^{-1})</th>
<th>( V_\text{T} ) cm(^3)g(^{-1})</th>
<th>( S_{\text{BET}} ) m(^2)g(^{-1})</th>
<th>( V_\text{T} ) cm(^3)g(^{-1})</th>
<th>Carbon (^{\text{a}}) wt. %</th>
<th>I(_d)/I(_G) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh</td>
<td>spent</td>
<td>fresh</td>
<td>spent</td>
<td>fresh</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>959</td>
<td>0.609</td>
<td>FD(^b)</td>
<td>FD(^b)</td>
<td>90.0</td>
<td>FD(^b)</td>
</tr>
<tr>
<td>MWCNT</td>
<td>406</td>
<td>1.100</td>
<td>110</td>
<td>0.291</td>
<td>96.2</td>
<td>96.1</td>
</tr>
<tr>
<td>G/AS700</td>
<td>287</td>
<td>0.634</td>
<td>221</td>
<td>0.841</td>
<td>14.5</td>
<td>1.4(^c)</td>
</tr>
<tr>
<td>G/AS900</td>
<td>286</td>
<td>0.630</td>
<td>224</td>
<td>0.831</td>
<td>14.9</td>
<td>2.0(^c)</td>
</tr>
<tr>
<td>FA/AS700</td>
<td>297</td>
<td>0.640</td>
<td>222</td>
<td>0.853</td>
<td>19.1</td>
<td>2.3(^c)</td>
</tr>
<tr>
<td>FA/AS900</td>
<td>281</td>
<td>0.597</td>
<td>223</td>
<td>0.835</td>
<td>20.3</td>
<td>2.4(^c)</td>
</tr>
<tr>
<td>FA/AS1100</td>
<td>215</td>
<td>0.549</td>
<td>207</td>
<td>0.744</td>
<td>17.0</td>
<td>2.3(^c)</td>
</tr>
<tr>
<td>AS</td>
<td>213</td>
<td>0.842</td>
<td>NM(^d)</td>
<td>NM(^d)</td>
<td>1.6(^c)</td>
<td>0.9(^c)</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by TGA (TGA patterns are compiled in Figs. S-1 to S-8); \(^{b}\) FD = fully decomposed during the catalytic run; \(^{c}\) Weight loss due to silica dehydroxylation; \(^{d}\) NM = not measured (as it shows very low activity); \(^{e}\) NA = not applicable.

For FA/AS900, FA/AS1100 and corresponding silica counterparts, the effect is very different. The isotherms of the silicas show inferior adsorption quantities, which is reflected in much lower surface areas than those of the hybrids; 281 versus 110 m\(^2\)g\(^{-1}\) and 215 versus 2 m\(^2\)g\(^{-1}\). The same holds for the pore volume. This is an indication of the enhanced stability against sintering of the silica in the hybrids.

These observations undoubtedly indicate that the thermal stability of the pure silica is very different from silica where a carbon coating is present; the carbon acts as a protective means against sintering. From this comparative study, it is concluded that hybrids can be prepared by pyrolysis up to 1100 °C retaining the mesoscopic texture. Therefore, 3 temperatures were considered for pyrolysis, ranging 700-1100 °C.
Figure 4. Nitrogen sorption isotherms at -196 °C for hybrid FA/AS materials (in red) including the corresponding calcined support (in black): a) 700 °C; b) 900 °C, and c) 1100 °C. Inserts corresponds to the BJH pore size distributions.
### 3.3.2 Structural and textural properties of the C/SiO\(_2\) hybrids, MWCNT, and AC materials

The carbon content of the hybrid materials was determined by TGA (Figs. S-3 to S-7, values in Table 3). The TGA patterns indicate that the total amount of organic content is between 14.5 and 20.3 wt.%, that is close to the nominal value of 15 wt.% (on carbon basis). The position of the maximum decomposition rate ranged between 575 to 625 °C, which shifts to higher temperatures with the applied pyrolysis temperature. MWCNT are almost purely formed by a carbon material with an inorganic residue of 3.8 wt. % (Fig. S-2, Table 3). The activated carbon (AC) shows a relatively high residue of 10 wt. % (Fig. S-1, Table 3), attributed to the binder. The maximum of the decomposition temperature of AC and MWCNT materials is relatively high, located at around 625 °C, at the applied heating rate of 10 °C/min.

The nature of the carbon species of the fresh materials was evaluated by Raman spectroscopy. The Raman patterns in Figure 5 reveal two broad absorptions centred at 1600 and 1310 cm\(^{-1}\), which are characteristic of amorphous carbon (G and D bands, respectively) [65,66]. Quantification of the intensity ratio (I\(_D\)/I\(_G\)), Table 3, reveals that the defective type of carbon is dominant with ratios ranging 1.3 to 1.9.

The isotherms of the furfuryl alcohol-based C/SiO\(_2\) hybrids were preliminary discussed in section 3.1 (Fig. 4); there is a reduction of the surface area with the pyrolysis temperature (297, 281 to 215 m\(^2\).g\(^{-1}\)); similarly the pore volume is reduced. Even at 1100 °C the hybrids contain a mesoscopic texture. A substantial fraction of micropores was detected (Table S-1) that explains the higher surface area of the FA/AS700 compared to AS-700, and in general that FA/AS700> FA/AS900>FA/AS1100>AS in terms of surface area. The glucose-based C/SiO\(_2\) hybrids have a similar texture, with an isotherm shape type IV with hysteresis H1, Fig. S-9. There is also a substantial fraction of micropores (Table S-1). For glucose, the pyrolysis temperature was screened at 700 and 900 °C (1100 °C pyrolysis temperature was considered to be of no interest for the glucose-based hybrids, as will be discussed later); no significant differences in the texture were noticed among these two pyrolysis temperatures. The presence of micropores is characteristic in all hybrid materials, while the thermally treated bare silica has negligible micropore volume (<0.006 cm\(^3\).g\(^{-1}\), in Table S-1). Therefore, the micropore volume was ascribed to be located in the carbon deposited layer; the micropores explain the higher surface areas of the hybrids compared to the bare silicas. All hybrid materials have a relatively narrow pore size distribution with the peak maxima located between 17.8 and 21.0 nm.
Figure 5. Raman spectra for the fresh carbon-based materials of the carbon-based materials under this study.

The texture of the structured MWCNT shows an isotherm type IV with hysteresis H1 as well (Fig. S-10). The texture is purely mesoporous as the micropore volume can be negligible (Table S-1). The pore size distribution (Fig. S-10, inset) has a main contribution of pores centered at 31.5 nm that is substantially higher than the hybrids; the high surface area is explained by the presence of small mesopores (3.0 nm) that are located in the inner space of opened tubes that contribute substantially to the surface area. The total pore volume is remarkably high with 1.1 cm$^3$.g$^{-1}$ compared to all other materials; this can also be deduced from the comparative over layer in Fig. S-11.

The texture of the activated carbon (Fig. S-10) is typical of a micro- and mesoporous material; isotherm type I with mesoporous hysteresis H2, displaying pore restrictions. The high surface area (959 m$^2$.g$^{-1}$) comes from the relatively high fraction of micropores that represents around 50% of the total pore volume (cf. values in Table 3 and S-1), while the pore volume (0.609 cm$^3$.g$^{-1}$) is comparable to the hybrids. These trends in surface area and pore volume can be deduced from Fig. S-11.

The TPO patterns (Fig. 6) can provide information about the stability under the harsh oxidative conditions of this reaction, eq. 2. From Fig. 6 it can be deduced that the thermal oxidative stability for the C/SiO$_2$ hybrids depends on the applied carbonization temperature and carbon source used.

With a higher applied pyrolysis temperature, the maxima of the oxidation pattern shift to higher temperatures, 582 up to 627 °C (FA samples) and 570 up to 613 °C (G samples). This is reasonable since the carbon becomes more graphitic with the increasing pyrolysis temperature, though this is not directly seen by Raman due to the heterogeneity of the materials displaying broad bands. All hybrids materials start to burn at higher temperatures than those of AC and MWCNT, at ca. 450-475 °C, while MWCNT and AC begin below 450 °C. From the TPO maxima, it seems that all carbon material could be stable, at least for short reaction times, under the oxidative conditions since the highest applied reaction temperature is 475 °C. The effect of time-on-stream (TOS) stability will be further discussed in the next section.
On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions.

3.3.3 Catalytic performance, characterization of the spent catalysts and oxidation stability

The ODH catalyst performance is given in Figure 7, where the EB conversion, ST and CO\textsubscript{x} selectivity as well as the overall ST yield are represented as a function of the time on stream. All the carbon-based materials are readily active and selective. They are all stable up to 15 h TOS. In this period, the hybrid catalysts are more active than AC and MWCNT. Among the hybrids the following trend in EB conversion was found: FA/AS700<G/AS900<FA/AS1100<FA/AS900<G/AS700. The selectivity of the hybrids varied considerably; the glucose-based hybrid renders very selective catalysts, higher than MWCNT and AC. The FA-based hybrids yield low ST selective catalysts; where the best values were found for FA/AS700, with selectivities in the range of the AC.

Figure 6. Oxidation rate patterns (TPO) for the carbon-based materials under this study. \( \alpha = (W_0 - W)/W_0 \); where \( W_0 \) is the initial weight. Conditions: synthetic air, 100 ml.min\textsuperscript{-1}, heating rate of 10 °C. min\textsuperscript{-1}.
Figure 7. Time on stream EB conversion (a), selectivity to ST (b), selectivity to CO\textsubscript{x} (c), ST yield, and (d) at various temperatures (475, 450, 425, and 450 °C) and O\textsubscript{2}/EB= 0.6 and 0.2 (vol.); GHSV of 3000 l/l/h; 10 vol. % EB. The top headings correspond to the O\textsubscript{2}:EB (vol.) ratio and reaction temperature in °C. It is noted that for low EB conversion (<15%) there were considerable errors in the ST/C\textsubscript{O\textsubscript{x}} selectivities leading to substantial noise; for the sake of clarity, some graphs are, therefore, plotted until 30 h TOS.

The selectivity to C\textsubscript{O\textsubscript{x}} is inversely coupled to ST (Fig. 7-c). This is because the selectivity to benzene/toluene and heavy condensates is much lower than C\textsubscript{O\textsubscript{x}}/ST and independent of the reaction conditions applied. It is noted that the selectivity values suffer from accuracy for low conversion; for the AS catalyst, the selectivity to ST and C\textsubscript{O\textsubscript{x}} summed up 80%, for EB conversions <5%, and no other by-products were detected (besides ~2% benzene and toluene).

After 20 h TOS the effect of the catalyst stability, against gasification/burning under the reaction conditions, becomes visible. The conversion and selectivity of all hybrid material severely decline until reaching a marginal conversion. For the glucose hybrids and FA/AS700 the EB conversion level down to the value found for the bare amorphous silica (AS in Fig. 7-a). The materials FA/AS900 and FA/AS1100 are relatively more stable with a steady EB conversion slightly above 10% after 60 h TOS. The selectivity also drops after 20 h TOS (Fig. 7-b) for all hybrids. It was observed that for low EB conversions (<15 %) the error is significant and the ST and
CO\textsubscript{x} selectivity scatter severely; because of that and for the sake of clarity, some graphs are only plotted until 30 h TOS.

Characterization of the spent hybrid catalysts after 60 TOS by TGA (Fig. S-3 to S-7; weight loss values are given in Table 3) shows that there is no carbon phase on the spent materials after the catalytic run. The materials became fully white and the weight loss detected by TGA (1.4-2.4 wt. %, 200-900 °C, Table 3) is attributed to surface Si-OH dehydroxylation. The texture of the spent samples is consistent with the carbon removal by gasification/burning under reaction. The textural parameters of all the spent hybrids are very similar, 221-224 m\textsuperscript{2}.g\textsuperscript{-1}, and comparable to the bare AS silica, 213 m\textsuperscript{2}.g\textsuperscript{-1}. Note that the porosity of the spent hybrids cannot be directly compared to the thermally treated AS materials (Table 2), because it was shown that the carbon stabilizes the silica against sintering. Performance and characterization clearly indicate that under limited O\textsubscript{2} (O\textsubscript{2}:EB=0.6) the effect of the gasification/burning is only visible after 20 h TOS.

The activated carbon (AC) is readily active and selective, with moderate EB conversion (27-30%) and ST selectivity (70-80%). This material is also gasified/burnt under reaction. The conversion goes to zero after 60 h TOS, though the selectivity remains high. Inspection of the catalyst bed after the run showed that the catalyst was completely consumed.

Nanostructured MWCNT starts with a relatively low EB conversion (~35 %) and moderate selectivity (~80 %); it is remarkably stable during the complete run. After 55 h TOS the conversion at 450 °C remained at ca. 33 %, the ST selectivity at 80 % and almost 20 % CO\textsubscript{x} selectivity. The high selectivity to CO\textsubscript{x} is a major handicap because it is waste product; reducing this parameter by making the catalyst more ST selective, or other useful by-products, such as benzene, toluene, can make MWCNT potentially interesting for EB ODH. The pronounced initial deactivation reported for nanotubes and ordered CMK-3 [26,51,54] was not observed for this Hyperion MWCNT, even starting at 475 °C. The textural properties of the spent catalyst are considerably reduced, and this is attributed to coke deposition or MWCNT modification, or both. The TGA derivative on the spent catalyst (Fig. S-2) shows two oxidation steps, one peak located at ca. 625 °C due to the oxidation of the original MWCNT and one centred at 550 °C associated to the oxygen-containing polyaromatic coke coming from the ODH reaction, or oxidized original MWCNT; both can be considered as ‘reaction coke’. Roughly 60% of the coke is associated to the reaction coke. It was found that the catalyst bed after the run was reduced in 20% in volume. The selectivity remains very stable while the EB conversion decreased steadily as a function of TOS; consequently the ST yield decreased steadily as well (Fig. 7-d).

It was tried to correlate the stability for all the catalysts with the TPO patterns. Neither the light-off temperature nor the peak maxima agrees with the observed reaction stability. The most stable catalyst under the reaction conditions, MWCNT, begins its oxidation at 450 °C, which is the lowest temperature in the series of materials. On the other hand, the temperature of the TPO maxima for AC and MWCNT nearly coincide, while the AC decomposes under the reaction conditions and MWCNT only partially. A plausible explanation could be that the carbon materials are formed by a heterogeneous mixture of amorphous and more crystalline domains. For instance, it is known that MWCNT contains amorphous domains at the outer surface or filling the inner cavity of the tubes; these amorphous domains burn at lower temperature. Such a lower stability has been used to purify nanotubes; air calcination purifies double-walled carbon nanotubes by burning the amorphous part [67]. Therefore, the TPO interpretation is troublesome since the amorphous domains are characteristic of the lower-temperature decomposition steps and can contribute to the peak maxima as well. In the case of the investigated MWCNT, it is reasonable to assume that the amorphous domains burn under the reaction conditions and can be attributed to the observed 20% volume reduction of the catalyst bed. The same
sample heterogeneity holds for the activated carbon and hybrid materials, based on the broad Raman spectra.

The stability was assessed from the apparent activation energies ($E_a$) of the air-assisted combustion process. This is because the apparent activation energy is related to the rate determining step, which by definition comes from the most stable domains of the carbon that resists more to the ODH conditions for a long run (i.e. in this case TOS>50h). Thus, this approach excludes the easily burnable coke associated to the light-off temperatures; the latter, a parameter that did not correlate to the observed catalyst life time, as discussed in the previous section.

The $E_a$ values were plotted for the different systems at 20 and 80% conversion level (Fig. 8). The $E_a$ increased with the pyrolysis temperature for the FA-based samples from 102(116) to 123(125) kJ.mol$^{-1}$, associated to the formation of more graphitic and stable carbon. The highest values were found for the AC and MWCNTs with 128(132) and 133(144) kJ.mol$^{-1}$; the values for the MWCNT are consistent with Frank et al., reporting an $E_a$ of 138 kJ.mol$^{-1}$ for unmodified CNTs [68]. The major differences in $E_a$ were found at 80% conversion, which is representative of the more stable carbon; it was found that the trend in the $E_a$ values (MWCNT > AC > FA/AS1100 > FA/AS900 > FA/AS700) fully agrees with the observed stability under the ODH reaction conditions (Fig. 7), which involve gasification and oxidation reactions. The $E_a$ values do not only give a quantification of the stability but also indicate about the low reactivity of the carbon species, which is in turn related to the low selectivity to CO$_x$. Since the fractions of benzene/toluene and heavy condensates are marginal (<2%) and independent of the reaction conditions, the low selectivity to CO$_x$ implies a higher selectivity to ST for the most stable carbons. This was observed in fact in this study for MWCNT compared to AC or hybrids (cf. profiles in Fig. 7-b). This ST selectivity and coke reactivity relationship indicates that CO$_x$ is formed through the deposited coke, instead of the complete oxidation of EB or ST to CO$_x$. These trends are consistent with previous work on aluminas [69,70]; where the most ST selective alumina showed a less reactive coke.

![Figure 8. Ozawa-derived apparent activation energies ($E_a$, kJ/mol) of the combustion at 20 and 80% conversions. Values are given in Table S-2.](image)

Overall, among the investigated carbon-based materials, nanostructured MWCNT has potential for EB ODH due to its higher oxidative stability when the deactivation or regeneration is remediated and the selectivity to CO$_x$ is reduced by enhancing further the oxidative stability.
On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions.

It is noted that an isothermal stability test at low temperature, e.g. 425 °C will only delay the gasification and full consumption of the catalytic material in view of the apparent activation energies, which clearly showed that the MWCNT is the most stable structure. A distributed oxygen feed to lower the local O₂ concentration, as recently reported by Nederlof et al. [71], would help in enhancing both ST selectivity and oxidation stability.

3.4 Conclusions

Carbon/SiO₂ hybrids, activated carbon and nanostructured MWCNT are readily active and selective in the oxidative dehydrogenation of ethylbenzene (EB), under industrially relevant conditions, implying concentrated EB feed, limited O₂ and a demanding reaction temperature range, 425-475 °C to assess gasification and combustion. All these materials are stable up to 15 h TOS. After this period, the gasification and burning phenomena take place; the hybrid materials decompose into their silica matrix, regardless of the applied pyrolysis temperature (700-1100 °C). A similar behaviour was observed for the activated carbon, whose bed is fully consumed after 60 h TOS.

MWCNT are exceptionally stable, no initial conversion decay was observed even at 475 °C, with an EB conversion of 33% and ST selectivity at 80 % at the end of the run. The selectivity does not decline during the run, though the EB conversion decreases steadily. This is attributed to ODH-derived coke deposition with a reduction of the surface area and pore volume. The 20% reduction of the catalyst bed volume is attributed to the gasification/burning of the more amorphous domains.

Interpretation of the reaction stability with light-off temperatures of the TPO patterns was not suitable due to the heterogeneous nature of the carbon materials, formed by amorphous and more crystalline domains. The apparent activation energies, however, correlate well to the catalyst stability.

In terms of the hybrid materials, it was learnt that the stability against thermal sintering of the amorphous silica is remarkably enhanced by the presence of a carbon coating, by suppressing the particle growth and phase transitions even at 1100 °C.

3.5 References

Chapter 3


On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions.


On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions.


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On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions.

Figure S-1. TGA pattern of the fresh AC catalyst. The material fully decomposes after the catalytic run and, therefore, no characterization could be carried out.

Figure S-2. TGA pattern of the fresh (in black) and spent (in red) MWCNT catalyst.
Figure S-3. TGA pattern of the fresh (in black) and spent (in red) G/AS700 catalyst.

Figure S-4. TGA pattern of the fresh (in black) and spent (in red) G/AS900 catalyst.
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Figure S-5. TGA pattern of the fresh (in black) and spent (in red) FA/AS700 catalyst.

Figure S-6. TGA pattern of the fresh (in black) and spent (in red) FA/AS900 catalyst.
Figure S-7. TGA pattern of the fresh (in black) and spent (in red) FA/AS1100 catalyst.

Figure S-8. TGA pattern of the fresh (in black) and spent (in red) AS catalyst.
On the stability of conventional and nano-structured carbon-based catalysts in the oxidative dehydrogenation of ethylbenzene under industrially relevant conditions.

**Table S-1.** Micropore volume for fresh and spent catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_m$ (cm$^3$g$^{-1}$) fresh</th>
<th>$V_m$ (cm$^3$g$^{-1}$) spent</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.316</td>
<td>FD$^a$</td>
</tr>
<tr>
<td>MWCNT</td>
<td>&lt;0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>G/AS700</td>
<td>0.019</td>
<td>0.001</td>
</tr>
<tr>
<td>G/AS900</td>
<td>0.018</td>
<td>0.001</td>
</tr>
<tr>
<td>FA/AS700</td>
<td>0.041</td>
<td>0.001</td>
</tr>
<tr>
<td>FA/AS900</td>
<td>0.038</td>
<td>0.001</td>
</tr>
<tr>
<td>FA/AS1100</td>
<td>0.019</td>
<td>0.003</td>
</tr>
<tr>
<td>AS</td>
<td>0.003</td>
<td>NM$^b$</td>
</tr>
<tr>
<td>AS-700</td>
<td>0.006</td>
<td>NA$^c$</td>
</tr>
<tr>
<td>AS-900</td>
<td>&lt;0.001</td>
<td>NA$^c$</td>
</tr>
<tr>
<td>AS-1100</td>
<td>&lt;0.001</td>
<td>NA$^c$</td>
</tr>
</tbody>
</table>

$a.$ FD = fully decomposed after the catalytic run; $b.$ NM = not measured; $c.$ NA = not applicable.

**Figure S-9.** Nitrogen sorption isotherms at -196 °C for the fresh glucose-based silica hybrid materials (G/AS). Bare silica is added for comparison. Inset includes the BJH pore size distributions. Isotherms for G/AS700 and G/AS900 are identical.
Figure S-10. Nitrogen sorption isotherms at -196 °C for the fresh MWCNT and AC materials. Inset includes the BJH pore size distributions.

Figure S-11. General overview of the nitrogen sorption isotherms at -196 °C for all materials (fresh).
Table S-2. The apparent activation energies of the combustion of fresh catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_a$ at 20% conversion kJ.mol$^{-1}$</th>
<th>$E_a$ at 80% conversion kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>128</td>
<td>132</td>
</tr>
<tr>
<td>MWCNT</td>
<td>133</td>
<td>144</td>
</tr>
<tr>
<td>FA/AS700</td>
<td>102</td>
<td>116</td>
</tr>
<tr>
<td>FA/AS900</td>
<td>122</td>
<td>124</td>
</tr>
<tr>
<td>FA/AS1100</td>
<td>123</td>
<td>125</td>
</tr>
</tbody>
</table>