Oxidative dehydrogenation of ethylbenzene under industrially relevant conditions

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Oxidative dehydrogenation of ethylbenzene to styrene over MWCNT. Regeneration: myth or reality?

Selectivity and activity are two important aspects in the oxidative dehydrogenation (ODH) of ethylbenzene (EB) to styrene. Besides those attributes, it is desirable that a catalyst is stable, or at least a regenerable, that can be used for a number of runs. Inorganic-based catalysts are easier to be regenerated by coking as the thermal stability is superior to carbon-based counterparts, though changes in texture and active sites can occur. These aspects imply that the material will have a limited life time, after that it must be recycled by a fresh batch. Despite the practical importance of stability, it is hardly found any study on regeneration of EB ODH-based catalysts.

In this work, two representative ODH-based catalysts (γ-Al₂O₃ and MWCNTs) have been studied regarding their regeneration towards coke removal by calcination. Before regeneration, the catalysts were exposed to EB ODH reaction conditions. Various regeneration strategies were investigated and the derived materials’ properties were characterized by physico-chemical methods, and those properties are compared to the fresh counterparts.
5.1 Introduction

Direct dehydrogenation of ethylbenzene (EB) in the presence of steam is the main way to produce styrene in industry. About 85% of styrene (ST) is produced by this way over a K-promoted Fe$_2$O$_3$ catalyst which is highly selective to styrene and stable [1,2]. The process takes place at temperatures as high as 580-630 °C [1], due to the endothermic thermodynamics and therefore suffers from high energy consumption. The conversion per pass is low due to the equilibrium limitations, involving a large recycle, and this has been the major driver to develop alternative ST production routes.

One of the aspects which can be improved is reducing the large amount of steam in the direct dehydrogenation reaction. Many efforts have been put forward to improve the process by making it steam-free and applying lower temperatures. The use of oxidants such as O$_2$ [3,4] is very promising as it helps to shift the reaction by H$_2$O formation. Therefore the oxidative dehydrogenations (ODH) have been thoroughly investigated, but it is not commercialized yet due to the limited catalyst stability and low selectivity to styrene.

The O$_2$-based oxidative pathway was originally studied on oxide-based carriers such as alumina [5]. It was shown that the coke deposited on the alumina’s surface under the oxidative conditions promotes the activity and selectivity [6-9] due to presence of Lewis acid sites. It was further proposed [10-13], and recently supported [14-16], that the formed coke acts as a selective and active site. Such type of coke has relatively high oxygen content (O:C=0.10-0.15 at.) and is considered to be polyaromatic.

Another family of catalysts that drew significant attention for the O$_2$-based EB oxidative dehydrogenation to styrene are carbon-based materials. Many types of carbon-based structures have been claimed to be active and selective, including activated carbons [17-30], onion-like carbons [31-33], carbon nanofibers [34-41], carbon nanofilaments [34], diamonds [28,30,33], graphite’s [19,34,38,42], MWCNT [28,30,40,32,33,42-49], and other types of carbons [50-52]. It is known that some of those materials, e.g. activated carbons, gasify/decompose under the reaction conditions [22,23,28,45]. The most stable ones are MWCNT. In a previous study, it was shown that it has a slow catalyst deactivation and good thermal stability under harsh conditions with the deposition of reaction-based coke [53]. Thus, MWCNT is a promising catalyst for the alternative ODH process.

Besides of activity and selectivity, it is desirable that a catalyst is stable, or at least a regenerable, that can be used for a number of runs. Inorganic-based catalysts are easier to be regenerated by coking as the thermal stability is high, though changes in texture and active sites can occur. These aspects imply that the material will have a life time, after that it must be recycled by a fresh batch. Despite the practical importance of stability, it is hardly found any study on regeneration of EB ODH-based catalysts.

In this work, two representative spent ODH-based catalysts ($\gamma$-Al$_2$O$_3$ and MWCNTs) have been studied regarding their regeneration towards coke removal by calcination. Before regeneration, the catalysts were tested under EB ODH conditions. Various regeneration strategies were investigated and the derived materials were characterized by physico-chemical methods and the properties are compared to the fresh counterparts.
5.2 Experimental methods

5.2.1 Materials

In this study a low SiO$_2$-stabilized $\gamma$-Al$_2$O$_3$ extrudates (Albemarle Catalysts BV, denoted as GA-F) and purified MWCNT (Hyperion CS-02C-063-XD, denoted as MW-F) were employed. The extrudates were crushed and sieved into a 212-425 μm fraction used for the catalytic tests and characterization.

5.2.2 Regeneration

Two regeneration protocols were carried out on the spent materials, mild and conventional. The mild regeneration (denoted as MR) was carried out in a quartz-tube housed tubular oven (Nabertherm RT 50/250-11). The sample was loaded in a flat quartz-based crucible that was placed horizontally in the centre of the furnace’s isothermal heating zone. The spent MWCNT (denoted as MW-S) and spent $\gamma$-alumina (GA-S) were regenerated at a temperature at 450 °C in 1% vol. O$_2$/Ar at a heating rate of 3 °C.min$^{-1}$ and held for 2, 5, 8, and 24 h for MWCNT. In the case of $\gamma$-alumina 5 and 24 h were applied. The conventional regeneration (denoted as R) was applied on the spent $\gamma$-alumina; this was done in the in LT9/11 Nabertherm box furnace at 450 °C in air at a heating rate of 3 °C.min$^{-1}$ and held for 5 h. Fresh, spent and regenerated materials with their codes and treatments are given in Table 1.

Table 1. Materials and their treatments

<table>
<thead>
<tr>
<th>Sample code $^a$</th>
<th>Material</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-F</td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>as-received</td>
</tr>
<tr>
<td>GA-S</td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>spent after reaction test, 60 h TOS</td>
</tr>
<tr>
<td>GA-R5</td>
<td>$\gamma$-Al$_2$O$_3$ spent</td>
<td>regeneration in air, 5 h</td>
</tr>
<tr>
<td>GA-MR5</td>
<td>$\gamma$-Al$_2$O$_3$ spent</td>
<td>mild regeneration in 1 %O$_2$/Ar, 5 h</td>
</tr>
<tr>
<td>GA-MR24</td>
<td>$\gamma$-Al$_2$O$_3$ spent</td>
<td>mild regeneration in 1 %O$_2$/Ar, 24 h</td>
</tr>
<tr>
<td>MW-F</td>
<td>MWCNT</td>
<td>as-received</td>
</tr>
<tr>
<td>MW-S</td>
<td>MWCNT</td>
<td>spent after reaction test, 60h TOS</td>
</tr>
<tr>
<td>MW-MR2</td>
<td>MWCNT spent</td>
<td>mild regeneration in 1%O$_2$/Ar, 2 h</td>
</tr>
<tr>
<td>MW-MR5</td>
<td>MWCNT spent</td>
<td>mild regeneration in 1%O$_2$/Ar, 5 h</td>
</tr>
<tr>
<td>MW-MR8</td>
<td>MWCNT spent</td>
<td>mild regeneration in 1%O$_2$/Ar, 8 h</td>
</tr>
<tr>
<td>MW-MR24</td>
<td>MWCNT spent</td>
<td>mild regeneration in 1%O$_2$/Ar, 24 h</td>
</tr>
</tbody>
</table>

$^a$. The suffix is related to the treatment: F (fresh); S (spent after the reaction cycle); R means conventional regeneration and MR mild regeneration; the number indicates the number of hours after reaching 450 °C.

5.2.3 Catalysts characterization

The organic content of the fresh and spent catalysts was quantified by thermogravimetric analysis (TGA) on a Mettler-Toledo analyzer (TGA/SDTA851e). The weight loss was monitored for a temperature program from 30 to 1000 °C at a heating rate of 10 °C/min using a flow of synthetic air of 100 mL.min$^{-1}$ NTP. Blank curve subtraction using an empty crucible was taken into account. The oxidation rate patterns (TPO) were obtained in the same instrument making use of the TGA derivative patterns.
The textural properties of the catalysts and the bare supports were analyzed by N\textsubscript{2}-physisorption at -196°C using a Micromeritics ASAP 2420. Fresh and regenerated \(\gamma\)-alumina samples were degassed at 300 °C for 10 h under vacuum. Spent samples were degassed at 200 °C for 10 h to ensure that the coke deposited on \(\gamma\)-alumina and carbon of MWCNT are not altered during the degassing. The surface area \((S\text{\textsubscript{BET}})\) was calculated with the standard BET method \cite{54} in the relative pressure range 0-0.25. The pore volume \((V\text{\textsubscript{T}})\) was calculated using the single point total desorption pore volume at the relative pressure 0.98. Pore size distributions were calculated using the BJH-model \cite{55}.

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

5.2.4 Catalytic tests

The catalytic tests were performed in a setup with six parallel quartz fixed bed reactors (inner diameter 4 mm) in down-flow operation. The reactors were loaded from top to bottom with a quartz wool plug, 10 cm glass beads (0.5 mm diameter), and 65 mm catalyst bed (0.80 ml) to ensure that the catalyst bed is located in the isothermal zone of the furnace. The glass beads have limited conversion which is less than 3% EB conversion under all applied conditions.

Each reactor gas feed has a flow of 36 ml/min (NTP) and consist of a mixture of nitrogen, oxygen, and ethylbenzene. A liquid ethylbenzene flow of 1 g.h\textsuperscript{-1} evaporates (3.6 ml.min\textsuperscript{-1} vapour at NTP) resulting in the 1:10 volume ratio of ethylbenzene and gas (10 vol.% EB) with a GHSV of 3000 l/l/h. The EB liquid evaporates in a \(\alpha\)-\(\text{Al}_2\text{O}_3\) filled tube in a synchronized flow with the gas feed. Pressure in the reactor system was 1.2-1.3 bars and an atmospheric outlet pressure drop was typically 0.2-0.3 bars.

The reactor outlet flows were analyzed using an online two channel gas chromatograph with a TCD (columns: 0.3m Hayesep Q 80-100 mesh with back-flush, 25m×0.53mm Porabond Q, 15 m × 0.53mm molsieve 5Å) for permanent gasses analysis (CO\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, CO) and a FID column (30 m × 0.53 mm, Df = 3 mm, RTX-1) for hydrocarbon analysis (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 \(O\textsubscript{2}/EB = 0.6\) and 0.2 (vol.). For all EB conversion data the oxygen conversion is 100%, unless otherwise is stated. All characterizations for the spent catalysts were done after the complete testing cycle of 70 h.

5.2.5 Regeneration efficiency of the carbon-based materials

The regeneration efficiency of the carbon-based materials was defined via the textural parameters \((\eta\text{\textsubscript{BET}}\text{\textsuperscript{Reg}})\), eq. 1) as the ratio between the final surface area, corrected by the weight loss during regeneration, to the initial surface area, which means the fraction of surface area that is recovered after regeneration or fraction that is lost, in case that this concept is applied to the spent catalyst:

\[
\eta_{\text{BET}}\text{\textsuperscript{Reg}} = \frac{S_{\text{BET}}\text{\textsuperscript{Reg.mat}}}{S_{\text{BET}}\text{\textsuperscript{Fresh}}} \times 100
\]

where \(S_{\text{BET}}\text{\textsuperscript{Reg.mat}}\) is the BET surface area of the regenerated material, \(S_{\text{BET}}\text{\textsuperscript{Fresh}}\) is the corresponding BET of the fresh sample and \(\Delta W\text{\textsuperscript{Reg}}\) is the weight loss during regeneration.
The total textural efficiency ($\eta_{\text{BET}}^{\text{Total}}$) contains the weight loss during the reaction:

$$\eta_{\text{BET}}^{\text{Total}} = \frac{\eta_{\text{BET}}^{\text{reg.mat}} \cdot \left[ 1 - \frac{\Delta W_{\text{ODH}}}{100} \right] \cdot \left[ 1 - \frac{\Delta W_{\text{Reg}}}{100} \right]}{S_{\text{BET}}^{\text{Fresh}}} \times 100 \tag{2}$$

$\Delta W_{\text{ODH}}$ is the weight loss or gain during the ODH reaction. For MWCNT in the applied catalyst run $\Delta W_{\text{ODH}} \approx 20\%$.

### 5.2.6 Regeneration efficiency of the alumina-based materials

This is defined as the corrected weight loss, relative to the bare alumina, from the TGA patterns as:

$$\eta_{\text{TGA}}^{\text{Reg}} = \left( 1 - \frac{\Delta W_{\text{spent}}^{X}}{\Delta W_{\text{spent}}^X - \Delta W_{\text{spent}}^X} \right) \times 100 \tag{3}$$

where superscript ‘$X$’ refers to any material (i.e. spent, regenerated, fresh). The recovery of the texture can be defined as:

$$\Delta S_{\text{BET}}^{\text{Reg}} = \frac{\Delta W_{\text{Reg}} \cdot S_{\text{BET}}^\text{reg.mat}}{S_{\text{BET}}^{\text{Fresh}}} \tag{4}$$

### 5.3 Results

#### 5.3.1 Catalytic tests

Figure 1 shows the catalyst performance of MWCNT (MW-F) and $\gamma$-alumina (GA-F) catalysts under relevant conditions, meaning a high EB concentration and limited $O_2$ with 20% excess compared to the stoichiometric amount. EB conversion, ST, $CO_x$ selectivity, and ST yield are plotted as a function of the time on stream (TOS). MWCNT is a readily active and selective catalyst at 475 °C, but $\gamma$-alumina requires approximately five hours to be active. However the conversion and selectivity of $\gamma$-alumina are higher. At the second temperature range at 450 °C during 20-40 h TOS, both catalysts have identical performance. The lowest temperature of the cycle (425 °C) shows higher activity and selectivity of MWCNT in comparison with $\gamma$-alumina, which makes it attractive for low-temperature ODH of EB to styrene in comparison with $\gamma$-alumina. At the end of the catalytic cycle, at 450 °C, conversion and selectivity are identical, and in agreement with step 2, though the conversion and selectivity values are lower due to deactivation. So the comparison of two steps at 450 °C shows that both catalysts deactivate in 2% for MWCNT and 5% for $\gamma$-alumina. Both catalysts demonstrate moderate stability, and MWCNT still have some advantages at low reaction temperature; higher activity and selectivity than alumina-based catalyst. The selectivity to $CO_x$ is inversely coupled to ST (Fig. 1-c). This is because the selectivity to benzene/toluene and heavy condensates are much lower than $CO_x$/ST and independent of the applied reaction conditions.
5.3.2 Spent catalysts

Temperature programmed oxidation was performed on the fresh and spent $\gamma$-alumina and MWCNT materials for the evaluation of the coke burning profiles (Fig. 2). The TPO profile of fresh MWCNT shows the presence of two types of coke which start to decompose at 400 °C and ends at 635 °C, with a maximum at 560 °C. It indicates a high thermal stability of the fresh MWCNT (Figure 2-a). TPO for the spent $\gamma$-alumina starts to decompose earlier at 400 °C, and it ends at 520 °C with a maximum at 460 °C (Figure 2-a) in a single step. Spent MWCNT has two contributions (I and II), which includes the multi-walled backbone (peak II), while the low-temperature peak (I) comes from a new type of carbon-based material that is deposited during the reaction (Figure 2-b), and it is ascribed to ODH-based polyaromatic coke.
The coke nature was investigated by Raman spectroscopy. The comparison of Raman spectra between fresh and spent MWCNT are shown in the Figure 3. The spectrum of the raw MWCNT material reveals two broad absorptions centered at 1600 and 1310 cm\(^{-1}\), which are indicative of amorphous carbon (G and D peaks). Raman spectrum of the spent catalyst indicates the presence of a more ordered structure that has been formed during the reaction. The D/G peak intensity becomes smaller and this can be explained by two possible effects: a) removal of the more amorphous carbon domains by gasification/burning and b) deposition of sp\(^2\)-rich carbon materials, or both effects; the latter is due to the buildup of new polyaromatic ODH coke.
The textural properties of the fresh and spent γ-alumina (Fig. 4) and MWCNT (Fig. 5) samples were investigated by N₂-physisorption analysis. The isotherm of fresh γ-alumina has a type IV with hysteresis H1 [56]. This type represents cylindrical pore geometry of solid particles with pore size equability and superficial pore connectivity. The hysteresis changes to H2 type for the spent γ-alumina (Fig. 4) with a closure point at 0.45 relative pressure. Hysteresis H2 [56] occurs in solids, where the pores have narrow necks and wide bodies or when the porous material has interconnected pores. The original material has no interconnectivity at 0.45 relative pressure, thus the pore neck restrictions of the spent sample is due to the excessive coke build-up. Pore size distribution curves of spent samples shift slightly towards low pore sizes that also indicates pore blockage. The specific surface area is depleted from 272 (GA-F) to 152-154 m².g⁻¹ (spent, Table 2) which is ~44% reduction. The spent sample was measured twice to ensure that sample is homogeneous; this was in agreement with TGA in terms of identical DTGA peak positions (Fig. 6-a, b) and residual weight losses (Table 2).
**Oxidative dehydrogenation of ethylbenzene to styrene over MWCNT.**

**Regeneration: myth or reality?**

Figure 4. Nitrogen sorption isotherms at -196 °C for the fresh and spent **Alumina samples**. Inset: BJH pore size distribution.

Figure 5. Nitrogen sorption isotherms at -196 °C for the fresh and spent **MWCNT materials**. Inset: BJH pore size distribution.
Figure 6. TGA curves of two spent $\gamma$-alumina (top) and two spent MWCNT (bottom). Conditions: synthetic air, 100 ml.min$^{-1}$, heating rate of 3 °C.min$^{-1}$. A) GA-S1; b) GA-S2; c) MW-S1; d) MW-S2. Peak I: ODH-based coke; peak II: MWCNT backbone.

Table 2. Texture properties of fresh, spent, and regenerated $\gamma$-alumina samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>$TGA$ (wt.%)$^a$</th>
<th>$n_{TGA}^{Reg}$ (-)</th>
<th>$S_{BET}^{Reg}$ (m$^2$.g$^{-1}$)$^c$</th>
<th>$V_T$ (cm$^3$.g$^{-1}$)$^c$</th>
<th>$\Delta S_{BET}^{Reg}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-F</td>
<td>3.9</td>
<td>1.00</td>
<td>272</td>
<td>0.639</td>
<td>1.00</td>
</tr>
<tr>
<td>GA-S1</td>
<td>31.5</td>
<td>0.00</td>
<td>154</td>
<td>0.231</td>
<td>0.57</td>
</tr>
<tr>
<td>GA-S2</td>
<td>31.7</td>
<td>-</td>
<td>152</td>
<td>0.223</td>
<td>0.56</td>
</tr>
<tr>
<td>GA-R5</td>
<td>3.7</td>
<td>1.01$^b$</td>
<td>259 (95)</td>
<td>0.646 (101)</td>
<td>0.95</td>
</tr>
<tr>
<td>GA-MR5</td>
<td>5.8</td>
<td>0.93$^b$</td>
<td>160 (59)</td>
<td>0.341 (53)</td>
<td>0.59</td>
</tr>
<tr>
<td>GA-MR24</td>
<td>3.3</td>
<td>1.02$^b$</td>
<td>256 (94)</td>
<td>0.650 (102)</td>
<td>0.94</td>
</tr>
</tbody>
</table>

$^a$ Determined by TGA weight loss between 200-800 °C; $^b$ Spent GA-S1 was employed for the regeneration study; $^c$ between parentheses the percentage of recovery is given, relative to the fresh counterpart.

Figure 5 shows the isotherms and pore size distribution of fresh and spent MWCNT. Fresh MWCNT has an isotherm type IV with hysteresis H1, which characterizes cylindrical pore geometry and relatively high pore size uniformity. Pore size distribution of the fresh MWCNT shows the presence of two peaks (Fig. 5, inset). The broad peak with a maximum of 30 nm is related to inter-rod mesopores and the small peak at 5 nm that can be related to smaller mesopores, likely from internal open tubes. Spent samples show much less adsorption capacity, due to the excessive coke build-up. In contrast to $\gamma$-alumina, the shape of the isotherm and hysteresis remain identical, of type IV H1, while the small peak at 5 nm pore size disappears. It
Oxidative dehydrogenation of ethylbenzene to styrene over MWCNT. Regeneration: myth or reality?

all indicates that the mesopores are blocked by the formed ODH coke during the reaction; however there is no indication of pore restrictions, due to the absence of low closure point. A duplo of the spent MWCNT was measured to account for sample homogeneity. The homogeneity of the spent MWCNT is lower than for γ-alumina; the BET varied in 7% while the pore volume in 16% (Table 3). This can be related to differences in ODH coke deposition along the reactor. Sample MW-S1 was employed for the regeneration studies. TGA patterns (Fig. 6) show two combustion steps; the low-temperature process (type I) is due to the ODH coke, while the higher temperature step originates from the burning of the MWCNT backbone, as discussed in Fig. 2-b. The comparison of the DTGA curves indicates that MW-S2 has a slightly higher fraction of the ODH coke than MW-S1, which is consistent with the lower BET and pore volume (Table 3).

Table 3. Texture properties of fresh, spent, and regenerated MWCNT samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>(S_{BET} ) (m(^2).g(^{-1}))(^a)</th>
<th>(V_T) (cm(^3).g(^{-1}))(^b)</th>
<th>(\Delta W^{loss}(%))</th>
<th>(\eta^{Reg}_{BET}(%))(^b)</th>
<th>(\eta^{Total}_{BET}(%))(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-F</td>
<td>406</td>
<td>1.100</td>
<td>-</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td>MW-S1</td>
<td>122</td>
<td>0.408</td>
<td>-</td>
<td>0.30</td>
<td>0.24</td>
</tr>
<tr>
<td>MW-S2</td>
<td>113</td>
<td>0.342</td>
<td>-</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>MW-MR2</td>
<td>312 (77)</td>
<td>0.544 (49)</td>
<td>9</td>
<td>0.77</td>
<td>0.61</td>
</tr>
<tr>
<td>MW-MR5</td>
<td>441 (109)</td>
<td>0.755 (69)</td>
<td>19</td>
<td>0.88</td>
<td>0.70</td>
</tr>
<tr>
<td>MW-MR8</td>
<td>453 (112)</td>
<td>0.708 (64)</td>
<td>38</td>
<td>0.69</td>
<td>0.55</td>
</tr>
<tr>
<td>MW-MR24</td>
<td>502 (124)</td>
<td>1.239 (112)</td>
<td>58</td>
<td>0.52</td>
<td>1.24</td>
</tr>
</tbody>
</table>

a. Between parentheses the percentage of recovery is given, relative to the fresh counterpart; b. In parenthesis, the regeneration efficiency of the pore volume is given.

5.3.3 Regeneration studies

For the regeneration of MWCNT, different regeneration times under mild conditions were applied to evaluate the recovery of the textural properties similar to the original material. Figure 7 shows a comparison between various regenerated MWCNT together with the fresh and spent materials. It is visible from the graph that MW-MR2 sample has higher adsorption capacity, a trend that continues with MR5 and MR8. Thus, increasing the regeneration time at the applied oxygen partial pressure, gives possibilities to reach the textural properties of the original material. Remarkably, 24 h of regeneration (MW-MR24) produces a material with better textural properties than the fresh MWCNT. This is also seen with a more intense PSD than fresh MWCNT, while the PSD maximum shifts towards higher sizes. In general, the pore size distribution after regeneration increases with increasing the regeneration time and the small peak at 5 nm appears back for the regenerate samples, except of MW-MR2. So, it demonstrates that 2 h is not enough to perform a good regeneration of the MWCNT. The derived textural properties are presented in the Table 3. It can be seen from the table that the spent MWCNT samples have 0.3 times its original surface area and ca. 0.4 times of the original pore volume. The BET of the regenerated increases notably and at 5 h (MR5) the BET surface area surpasses that for the raw material up to a factor 1.24 for the 24 h-regenerated sample. The pore volume is also recovered, but it does not arrive to the original MWCNT’s quantity, with the exception of the 24 h that is a factor 1.12. The situation with the MR24 can be attributed to the fact that the regeneration can also clean the MWCNT backbone by removing amorphous material; therefore the final material is more porous. Thus, from this study, it is concluded that both, BET and pore volume can be recovered after a mild regeneration. To make the comparison complete, the weight loss due to the regeneration itself must be considered. This is considered in
equation 1, where the regeneration efficiency based on the BET surface area and weight loss is defined. When using this parameter, an optimal value is found. The regeneration efficiency increases from 0.77 (MR2) with a maximum of 0.88 at 5 h regeneration, and then decreases for 8 and 24 h. This information indicates that because of the weight loss, the surface area cannot come back to the original value due to the weight loss; it also concludes that the optimal conditions in terms of BET surface area are 5 h. A second factor that affects the overall regeneration efficiency is the weight loss associated to the ODH reaction itself; the total regeneration efficiency is defined in eq. 2 that accounts for the reaction weight loss. The consequence of this is the lower regeneration efficiency with a maximum of 0.70 for MR5. This means that under the optimal conditions of regeneration, 30% of the total surface area is lost due to the reaction plus regeneration.

Figure 8 shows the oxidation rate patterns for the fresh, spent, and mild-regenerated samples for the MWCNT. It is clear from the figure that the peak of the spent catalyst at ca. 520 °C disappears with the increasing regeneration time. The first peak of the spent catalyst disappears completely after regeneration for 24 h. The maximum of the regenerated samples’ peak shifts to 580 °C. It demonstrates that the coke which was formed on the MWCNT is removed upon regeneration, while the MWCNT structure remains unmodified with improved thermal stability.

The regeneration was also studied regarding the \( \gamma \)-alumina after the ODH reaction under identical conditions. It is expected that \( \gamma \)-alumina can be easily regenerated. The isotherms and pore size distribution curves of GA-R5 and GA-MR24 are nearly identical to the fresh \( \gamma \)-alumina (Fig. 9), meanwhile the isotherm and PSD for GA-MR5 show less adsorption due to the incomplete regeneration. The TGA-based regeneration efficiency for the MR5 was about 93% but this 7% left residue impacted on the BET with 41% lower than the fresh counterpart (Table 3). However, the regeneration in air for 5 h or 24 h in air gives rise to 95 and 94% recovery of BET surface area and approximately 100% pore volume’s recovery, with no residual coke (Table 3).

**Figure 7.** Nitrogen sorption isotherms at -196 °C for the fresh, spent, and regenerated MWCNT at different conditions. See Table 1 for description of the treatment conditions. Inset: BJH pore size distribution.
MWCNT and γ-alumina show similar performance in the oxidative dehydrogenation of ethylbenzene to styrene and demonstrate good stability under the applied conditions; the selectivity is however relatively lower compared to the conventional process. Both types of materials suffer from coke deposition, under the reaction conditions, that depletes the textural features notably. γ-alumina can be fully regenerated by calcination in air, or longer times under milder conditions, with the
complete recovery of its textural features and no residual coke. MWCNT can also be regenerated under mild conditions. This was possible because the deposited ODH coke has a lower reactivity, i.e. appears in the TPO profiles at lower temperatures, than the MWCNT backbone. In order to quantify the regeneration efficiency, the weight loss during the regeneration and reaction conditions have been taken into account. At the optimal conditions, 70% of its initial surface area can be recovered. It was also found that the specific surface area, for prolonged regeneration times, can be even higher than the starting material. This was explained by the cleaning effect of the MWCNT backbone from amorphous domains, at the expense of a substantial weight loss. Therefore, MWCNT can not be considered a single-use material, but can be partially recycled.

5.5 References


Oxidative dehydrogenation of ethylbenzene to styrene over MWCNT.

Regeneration: myth or reality?


