5. Oxidative Dehydrogenation experiments

Cleaved and activated (oxygen-sputtered) HOPG samples were exposed to activity testing using the previously-mentioned microflow reactor.

5.1 Oxidative dehydrogenation reaction over cleaved HOPG

Figure 5.1 shows the catalytic activity of freshly-cleaved HOPG sample at two different temperatures expressed by the percentage yield of styrene versus time on stream.

It can be seen that this sample has a very low catalytic activity resulting in a percentage yield of styrene in the range of 0.2 – 0.3 % at 400 ^{o}C, which increases to about 0.55 % upon increasing the temperature to 450 ^{o}C.
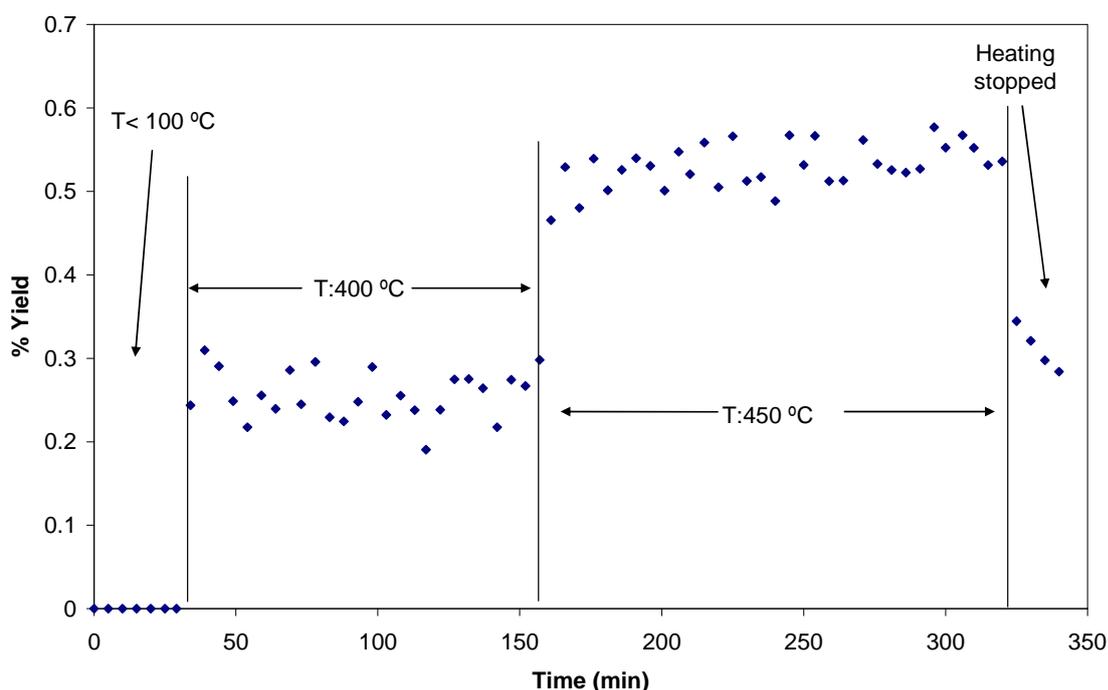
Figure 5.1. Reaction over cleaved HOPG (20 ml/min, 1:1 O2/EB, ~ 1 % EB, rest He)

Figure 5.2 shows a reaction experiment over another freshly cleaved HOPG sample in which the oxygen/EB ratio was changed during reaction at 400 ^{o}C. The oxygen/ethylbenzene ratio ranges from zero to 2.6. Upon decreasing the oxygen/ethylbenzene ratio from 1.3 to 0.65, a slight decrease in the conversion can

be seen. More clearly, the conversion converges to zero upon switching to oxygen-free reaction stream. However increasing the oxygen/ethylbenzene from 1.3 to 2.6 does not show a clear influence of the activity.
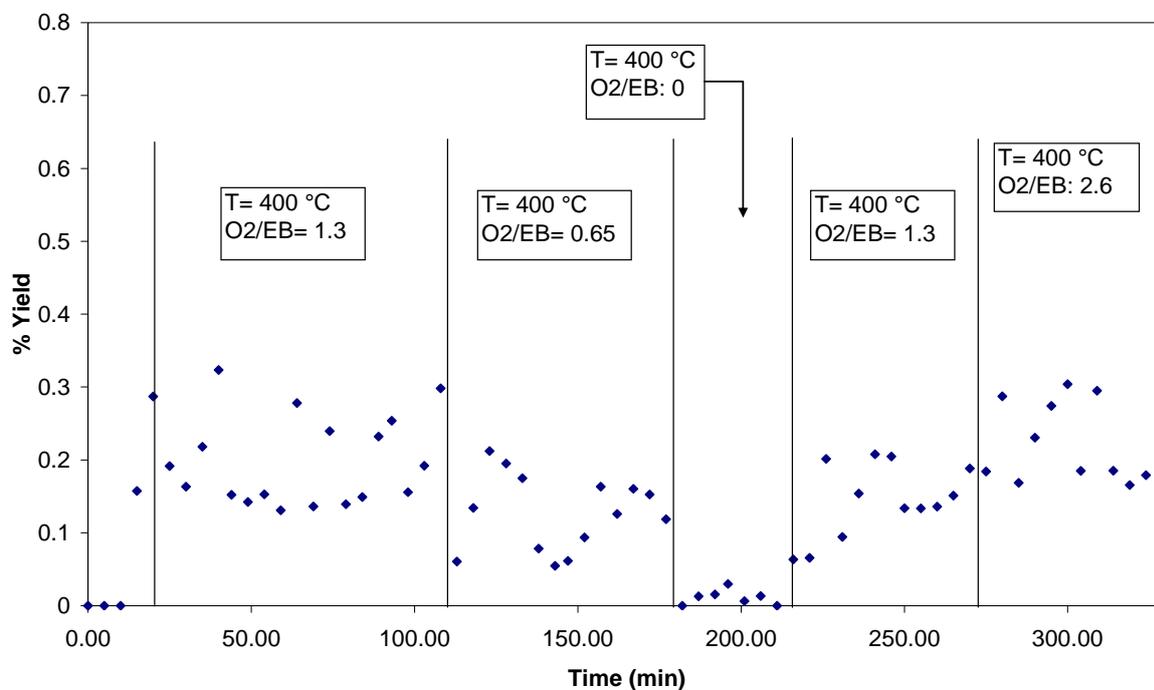
Figure 5.2. Reaction over Fresh HOPG

Vanishment of the apparent activity in the case of oxygen-free reaction feed is a clear evidence of an oxidative dehydrogenation process and proves that the apparent low conversion is a result of catalytic activity and not a background signal.

In view of the very low conversion, it can be concluded that the oxygen loading is more than what is needed for the reacted amount of EB, even at the lower tested limit of 0.65 O_2/EB. Thus, changing this value does not have a large influence on the conversion. Another point which should be considered here is the high standard deviation of the measurement points which is mainly caused by the fact that the produced amount of styrene is very low and is just above the detection limit of the used micro GC system. Figure 5.3 shows the produced GC peak of styrene at a percent yield of 0.5%. This fact makes the styrene signal highly affected by the signal noise and increases the standard deviation of the data points.
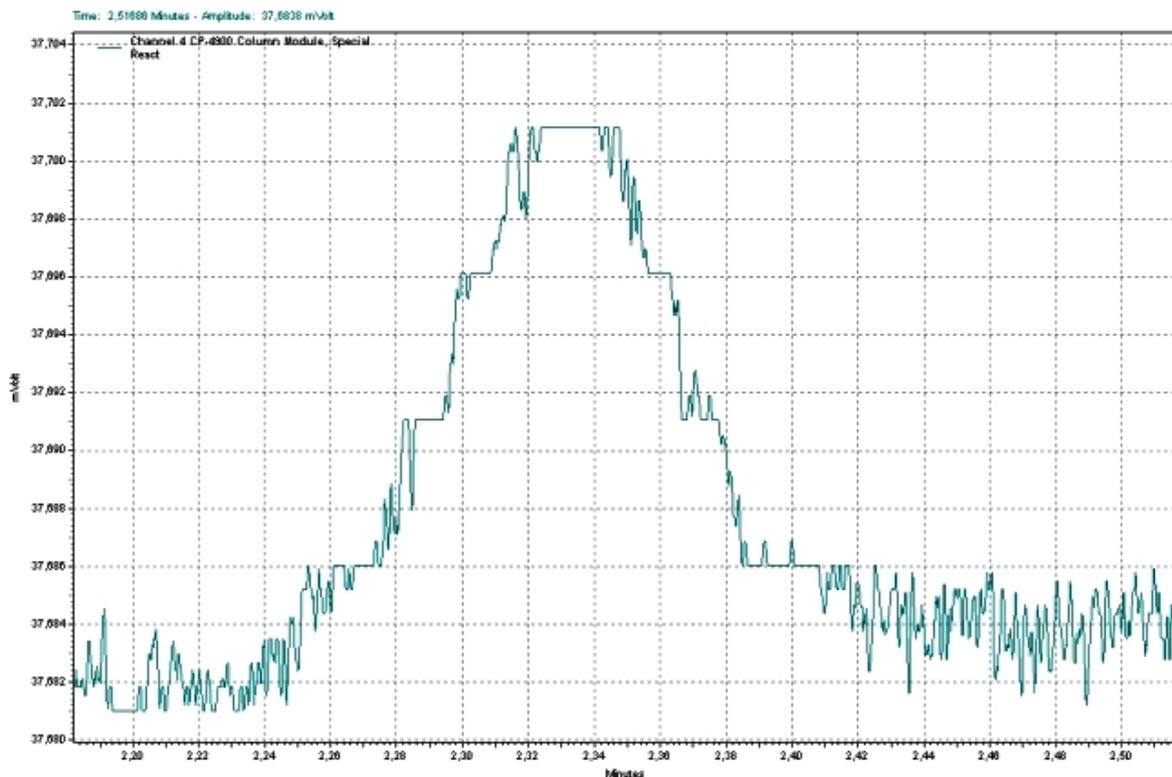
Figure 5.3. GC styrene peak at a percentage yield of 0.5 %

5.2 Oxidative dehydrogenation reaction over oxygen-sputtered HOPG

Figure 5.4 shows the activity measurement over oxygen-sputtered (30 min, 1.5 µA, 1 keV) sample. The measured percentage yield varies from about 0.3 % at 400 ^{o}C to 0.55 % at 450 ^{o}C. Unexpectedly, the observed activity of this sample lies in the same range observed for the freshly cleaved HOPG sample (although the mean value is higher). This finding puts the sensitivity of our experimental system under doubt. A reasonable reason for the similar observed activities could be that the used system is –for some reason- unable to sense the samples catalytic activity.

To elucidate the reason for the apparent similar activities of cleaved and oxygen sputtered HOPG, it was necessary to check the ability of our experimental system to detect the catalytic activity of samples under analysis.
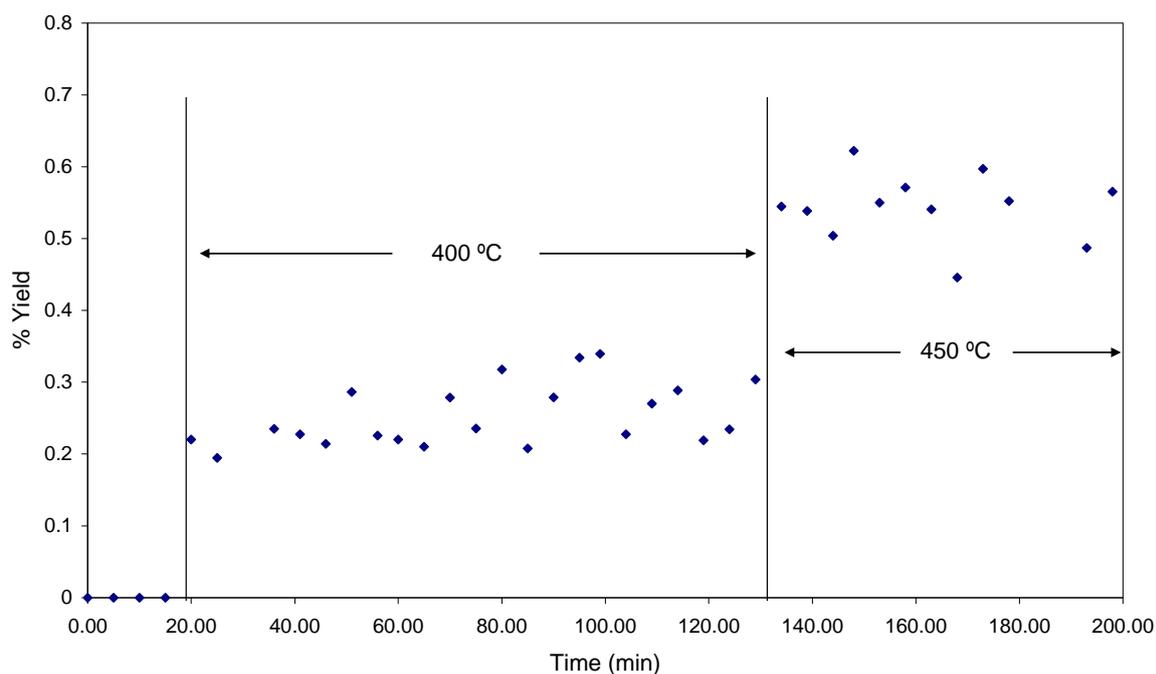
Figure 5.4 Reaction over oxygen-sputtered HOPG (O_2/EB = 1.3).

5.3 Oxidative dehydrogenation reaction over CNT samples

To check the sensitivity of the experimental system, a sample which is known to be active was tested using our experimental setup, we chose for this purpose carbon nanotubes sample which was tested by other laboratories and found to have high catalytic activity in ODH of ethylbenzene. Different amounts of this CNT were deposited as a thin layer on the surface of HOPG substrates and steel substrates. These samples were then used to perform catalytic activity measurements.

Figure 5.5 shows the activity of a sample containing 0.09 mg of CNT sample, the measured percentage yield for this sample varies between 0.25 % at 400 ^{o}C and 0.6 % at 450 ^{o}C. This apparent activity is still in the same range observed for both the cleaved and the oxygen-sputtered HOPG samples tested in the previous sections.

Another sample containing higher amount (0.19 mg) of carbon nanutubes was then tested. As can be seen in figure 5.6, the apparent percentage yield for this sample ranges from 0.45 % at 400 ^{o}C to 1.6 % at 450 ^{o}C, which is the double of what observed so far.
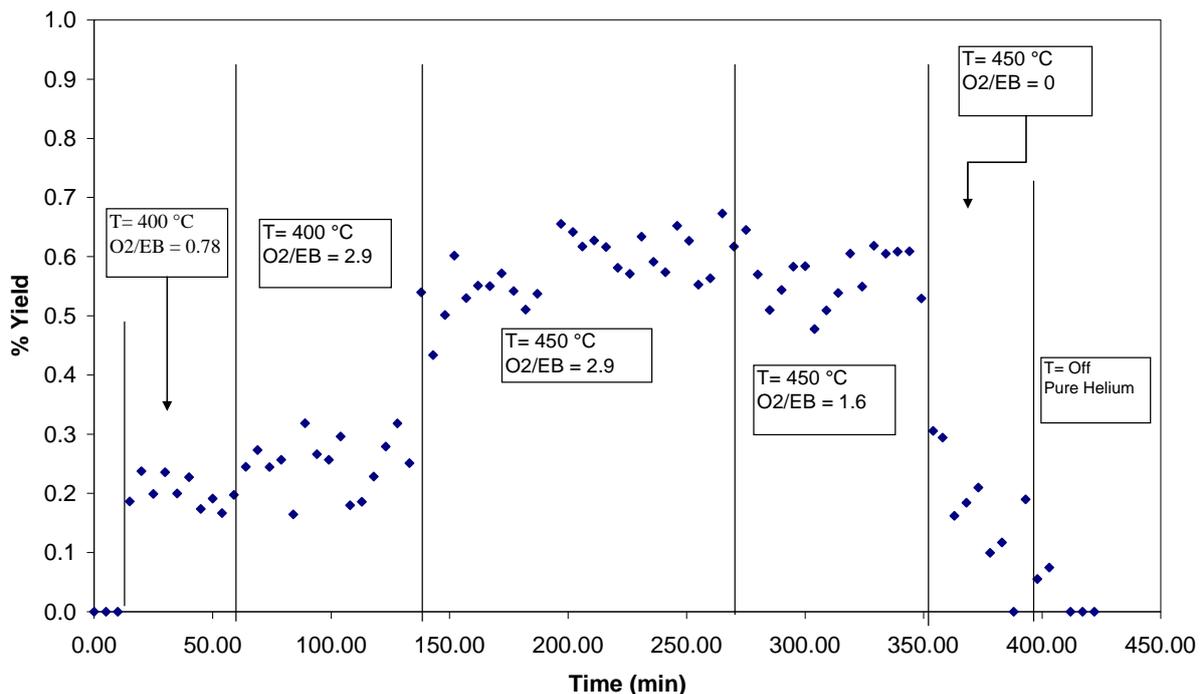
Figure 5.5 Activity of carbon nanotubes over HOPG substrate. CNT content: 0.09 mg, BET surface area=49.32 cm^2

These observations give an obvious evidence that the used experimental system is capable of detecting and quantifying the catalytic activity in the expected range of the samples under investigation.
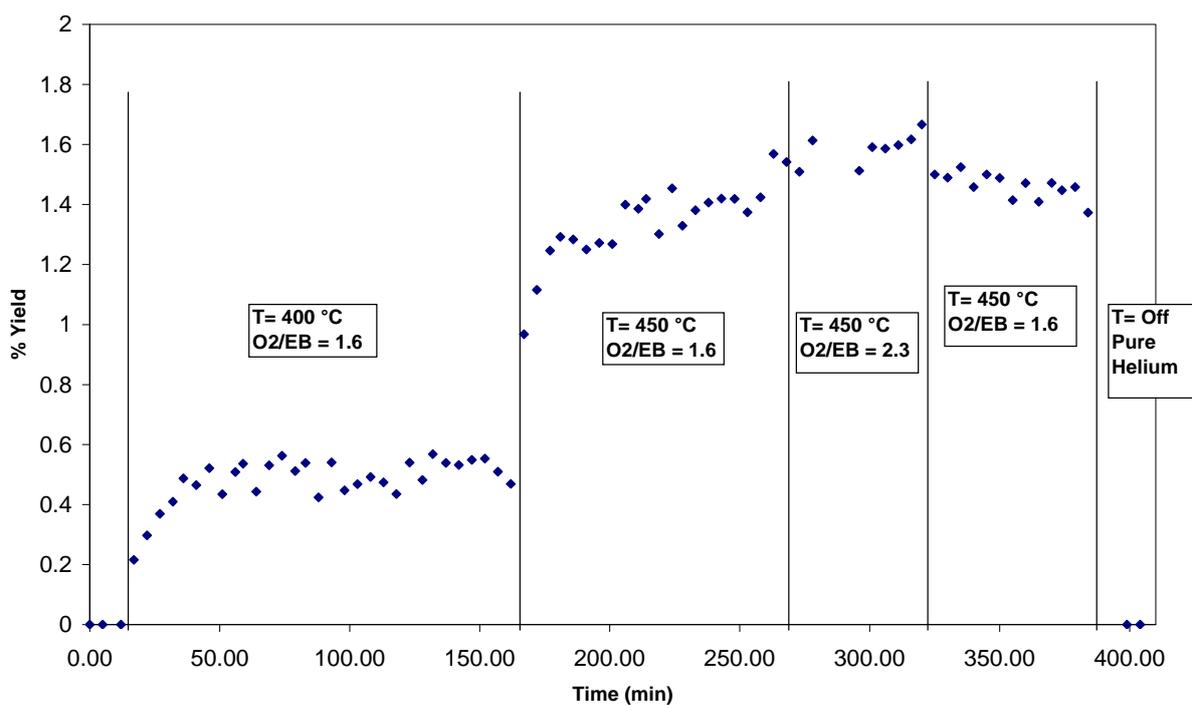
Figure 5.6 Activity of carbon nanotubes over HOPG substrate, CNT content: 0.19

mg, BET surface area=104 cm^2

As another proof of that fact, the sample containing 0.09 mg of CNT was loaded with additional amount of CNT, before its activity was re-tested and found to be higher than before increasing the amount of CNT. This is shown in figure 5.7
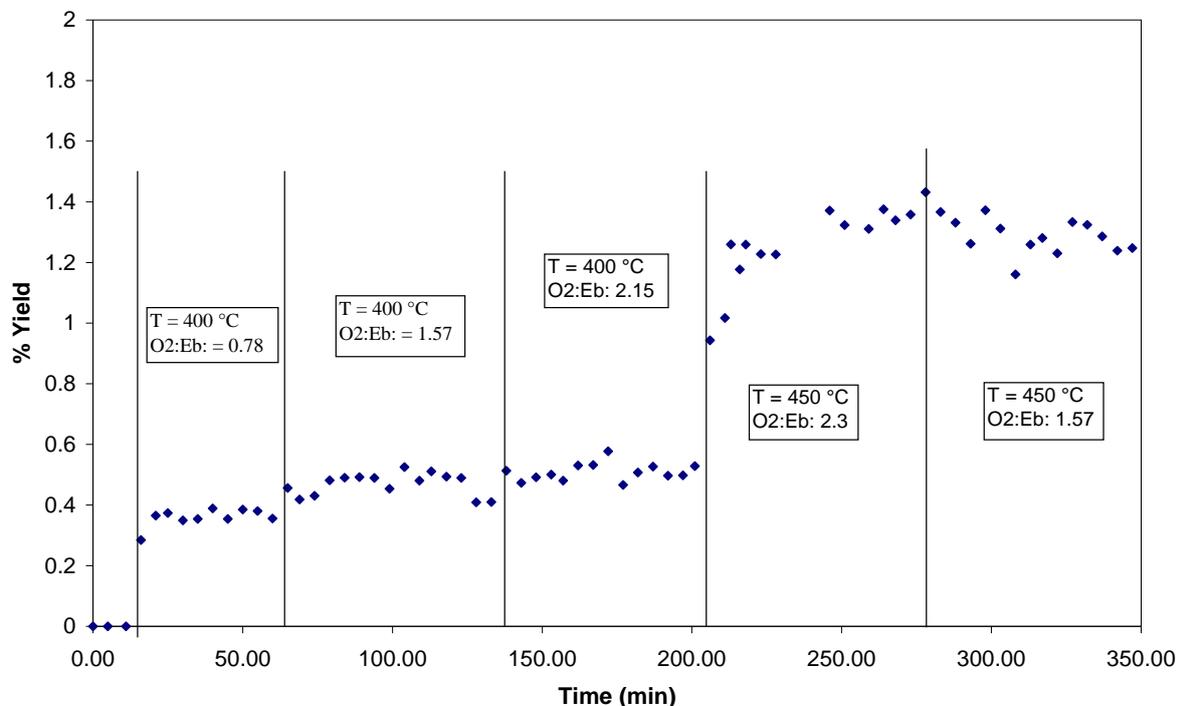
Figure 5.7 Activity experiment of CNT/HOPG
Sample: CNT sample 1(containing 0.09mg CNT) + added amount of CNT (0.17 mg), Total amount: 0,26 mg, BET Area=145 cm^2

Carbon nanotubes samples were also tested as a thin layer over steel substrates. Figure 5.8 shows the measured activity of a sample containing 0.22 mg CNT deposited over steel disk. Surprisingly, the catalytic activity of this sample was about one order of magnitude higher than that observed for all previously tested samples. The measured percentage yield was found to range from about 5 % at 400 ^{o}C to 9 % at 450 ^{o}C.

This result presents another proof of the detection capability of our experimental system. However, considering the measured activity of CNT/steel sample, it is not clear if this detected high activity in the last sample is a result of a catalytic system produced by the interaction of carbon nanotubes with the steel surface, or a simple summation of the activity of each of the systems (CNT and Steel) alone. To elucidate that, the activity of the clean steel substrate was tested.

Reaction CNT/Steel
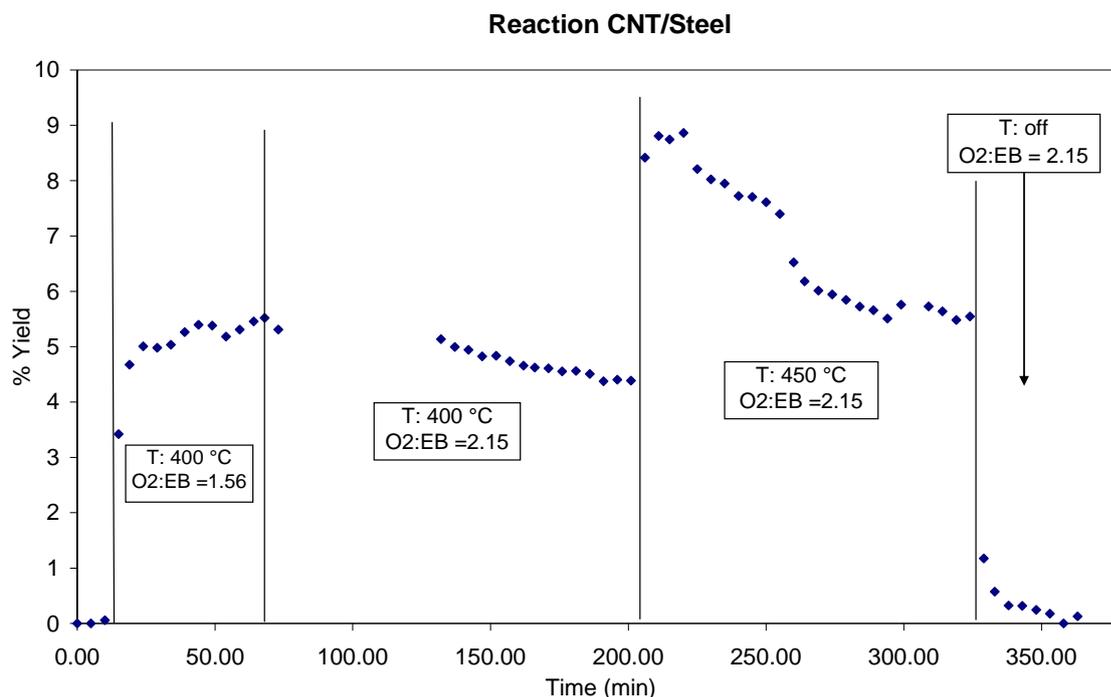
Figure 5.8 Activity of CNT/Steel sample CNT contant: 0.22 mg

In Figure 5.9 the activity of a clean steel substrate is shown. The observed percentage yield of this sample is 3.5 % at 400 ^{o}C at the beginning of the experiment. The activity decreases with time and percentage yield reaches about 2.5 after 150 minutes of time on stream. Increasing reaction temperature to 450 ^{o}C at this point doubles the observed activity. It jumps to reach a value of 4.2 %.

If we consider the initial activity of this sample, it is about 1 % less than that of CNT/steel sample. This difference of 1 % is in the expected range of the activity of CNT sample alone (in the light of the results of CNT/HOPG samples).

The last observations suggest a simple combination of the activities of CNT and steel when used together. On the other hand, the deactivation behaviour of the clean steel substrate looks different from that of CNT/Steel. Steel substrate loses about 40 % of its activity within 150 minutes of time on stream at 400 ^{o}C, while CNT/Steel sample looses no more than 10-15 % after 200 minutes of time on stream at same reaction conditions. It could be concluded that the presence of carbon nanotubes on the steel sample decelerates its deactivation. No certain mechanism can be concluded, but as

reported in the literature dealing of carbon deposits building during ODH of ethylbenzene[1,2], sample nature plays a significant role in the rate of building and the nature of carbon depositions on the catalyst surface, which is the main reason for the deactivation of steel. It seems that carbon nanotubes either hinders the building of carbon deposits on the steel surface or plays a role in building carbon deposits with higher activity than those built in the case of steel alone. Anyway, this issue lies beyond our current research interests and no more investigations were performed.
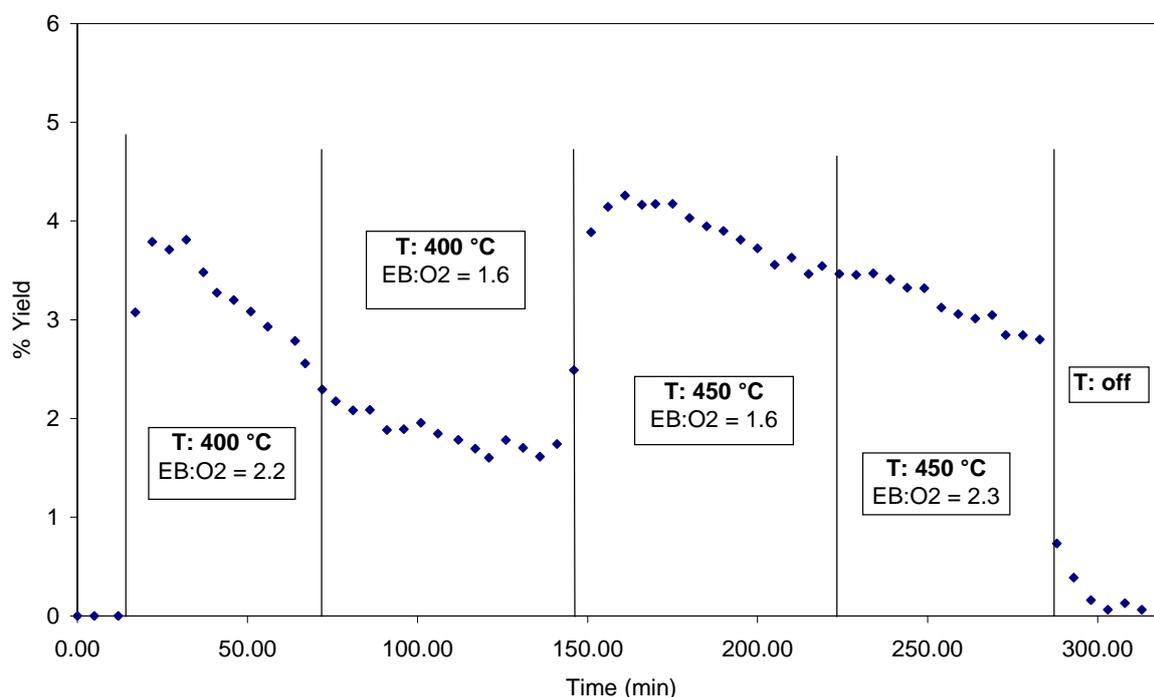
Figure 5.9 Activity measurement of steel sample

Finally, and before confirming the initial observations about the similar detected activities of cleaved and oxygen-sputtered HOPG, it was necessary to exclude the possibility of any sudden –unnoticed– change that may have affected the experimental system during last experiments and made it more sensitive.

5.4 Repeated oxidative dehydrogenation reaction over HOPG sample

To confirm the obtained activity results of HOPG samples, the activities of cleaved HOPG sample and that of an oxygen-sputtered sample were measured again at different temperatures. Figure 5.10 and Figure 5.11 show the activity measurements of cleaved HOPG and oxygen-sputtered HOPG samples, respectively.

The measurements for both samples were performed at four different temperatures (400 ^{o}C, 425 ^{o}C, 450 ^{o}C and 480 ^{o}C). Both samples showed nearly identical activity behaviour. The observed percentage yield at 400 ^{o}C was found to be about 0.2 % which increases slightly reaching 0.25 - 0.3 % at 425 ^{o}C. Increasing the temperature to 450 ^{o}C, raises the percentage yield to 0.35 – 0.4 %. At 480 ^{o}C, the percentage yield increases to be between 0.55 – 0.6 %.

This data was used to determine the apparent activation energy (Arrhenius) for both processes, it was found to be 54 +/- 8 kJ/mol and 51 +/- 9 kJ/mol for the cleaved sample, and the oxygen-sputtered sample respectively.
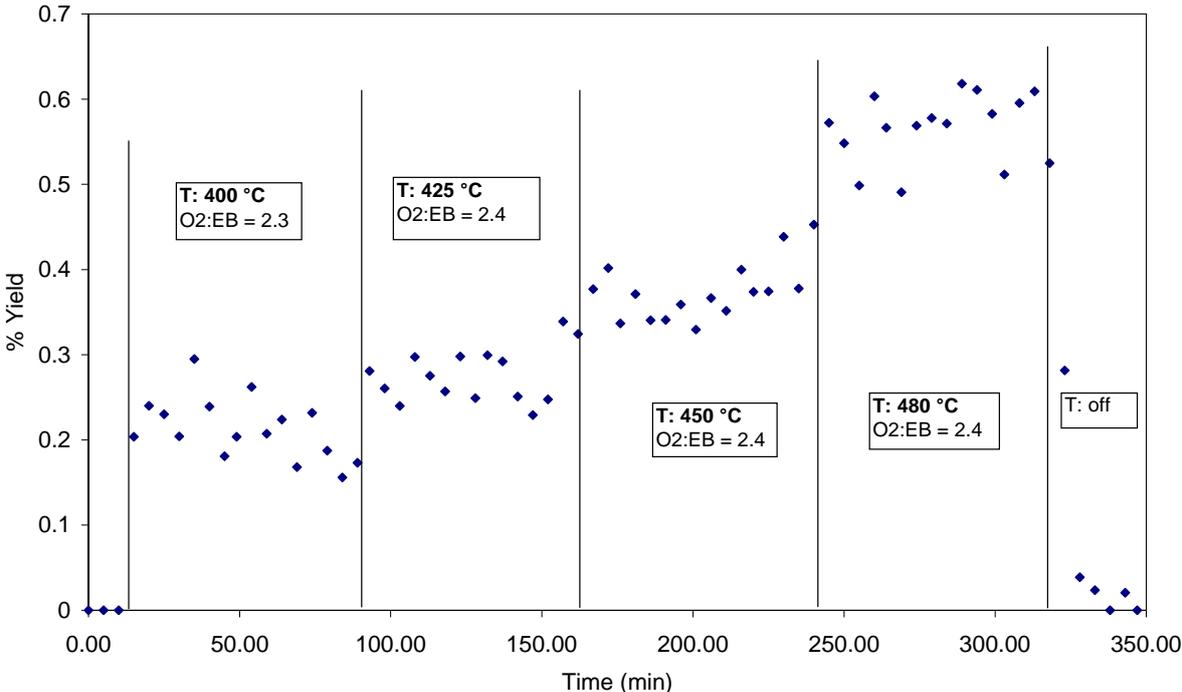
Figure 5.10. Activity of cleaved HOPG sample
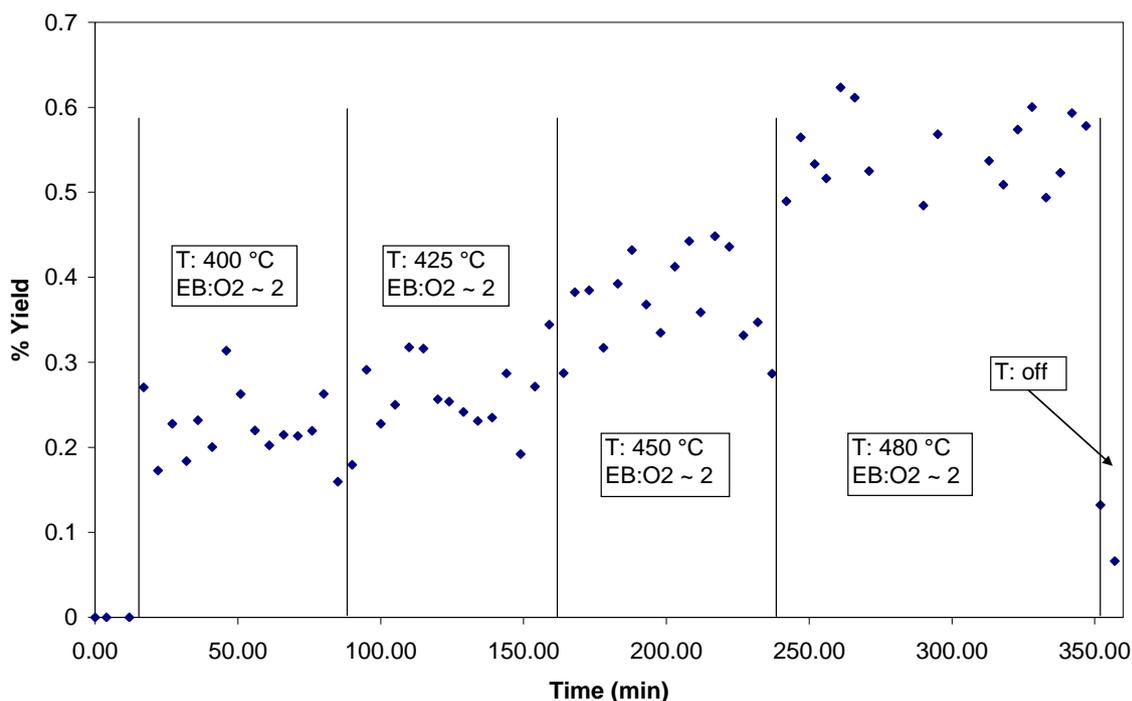
Figure 5.11. Activity of oxygen-sputtered HOPG sample (30 min, 1.5 µA,1keV)

At this point we can be confident about the results obtained for the catalytic activity of both the cleaved and the oxygen sputtered HOPG sample, but before discussing the similar activities of these samples, the following question should be considered. Does this very low activity imply that HOPG is not good as a model catalyst?

5.5 Is it right to consider HOPG as a model catalyst for ODH reactions over carbon materials?

To answer this question, it is useful to compare the observed activity with some other active carbon materials at same conditions. Onion-like carbon, which was reported to be superior to other catalysts in the ODH of EB, was taken as an example. The conversion data obtained for this material[3] was used for that purpose.

A percentage yield of styrene of 62 % was reported using this material at 515 °C. Using the available activity data at different temperatures available in the same source, the extrapolation was used to calculate the reaction rate at 450 °C. The value for onion-like carbon was found to be $1.1 \times 10^{+10}$ molecules.s^{-1}.cm^{-2}.

For HOPG, the reaction rate at 450 $^{\circ}$C (0.35 styrene % yield) was found to be ~1×10^{14} molecules.s^{-1}.cm^{-2}.

It is clear that the reaction rate obtained with HOPG is much higher than that with the OLC but it is important to mention here that direct comparison is not possible because of the transport limitations encountered in the case of OLC taking into account the porosity of this material. Such a limitation is absent in the case of HOPG, However, this result indicates that the obtained (low) activity observed for HOPG samples is already significant and indicates the possibility and correctness of using HOPG as a model catalyst for other carbon materials. Nevertheless, some experimental parameters including the reactant concentration and flow rate should be re-adjusted.

Finally, the similar activity behaviour of cleaved and oxygen-sputtered HOPG samples can have different explanations such as:-

1. The building of carbon depositions on the samples after a short time of reaction, this time should be very short (less than the response time of the experimental setup) that our setup was unable to see the initial activity. In this case, we had to assume that the oxygen-sputtered sample has higher initial activity which disappears quickly by the building of (less active) carbon depositions.

2. It is possible that the majority of the functional groups on the surface are not of that type required for ODH reactions: It is suggested that only carbonyl/quinine/hydroxyl groups play a role in ODH reactions over carbon materials[4-6]. It is possible that oxygen sputtering of HOPG was not efficient in creating the needed oxygenated groups.

More investigation of this issue is required to achieve more knowledge and better understanding.

(1)   A. Guerrero-Ruiz; Rodriguez-Ramos, I. *Carbon* **1994**, *32*, 23-29.
(2)   Lisovskii, A. E.; Aharoni, C. *Catalysis Reviews* **1994**, *36*, 25-74.
(3)   Maksimova, N. PhD-thesis, TU-Berlin, **2002**.

(4)   Pereira, M. F. R.; Orfao, J. J. M.; Figueiredo, J. L. *Applied Catalysis A: General* **1999**, *184*, 153-160.

(5)   Cadus, L. E.; Gorriz, O. F.; Rivarola, J. B. *Ind. Eng. Chem Res.* **1990**, *29*, 1143-1146.

(6)   D.S.Su , N. M., J.J.Delgado, N.Keller, G.Mestl, M.J.Ledoux, R.Schlogl *Catalysis Today* **2005**, *102–103*, 110 –114.