

7. Conclusions

In the study of oxygen interaction with HOPG, it was clear that this material is not easily attacked by molecular oxygen. Even after argon sputtering, no evidence was seen for the interaction between the surface and molecular oxygen. However, oxygen-sputtering was able to introduce oxygen to the surface; this was confirmed with AES, XPS and TPD spectroscopies. TPD spectra were characterized by a low-temperature CO₂ desorption peak, and a high-temperature CO desorption peak. XPS gave evidence for two or more different oxygen complexes on the surface. However, the nature of this surface oxygen and the way it binds to the surface could not be identified in our experiments.

An unexpected event was the appearance of a second high-temperature desorption peak of CO after several O₂-sputtering-anneal cycles. The absence of any AES signal of this oxygen is not understood, but the most probable reason would be that it is bound in pores deep in the sample which makes it invisible for AES. Additionally, the surface became active towards molecular oxygen after the appearance of this high-temperature peak. This indicates a significant damage of the structure accompanied by production of reactive sites.

It is not clear if these reactive sites are found by the influence of accumulative oxygen sputtering alone or by the influence of repeated sputtering-anneal treatments. This, in addition to the relation of this peak to the activity of HOPG are a subject for further studies.

In the reactivity testing of cleaved and oxygen-sputtered HOPG sample, it was proven that both cases reveal nearly the same activity in the oxidative dehydrogenation process of ethyl benzene. The observed activity was in the range of 0.2 – 0.6 percentage yield of styrene depending on the used temperature. The activity originates definitely from the carbon structure itself because the used material (HOPG) is metal free.

The observed activity was confirmed to result from the ODH process; this was clear by the disappearance of the activity upon switching to an oxygen-free reaction mixture or by switching off the heating. Any experimental system failure was excluded by performing reactions using known active material (carbon nanotubes).

Possible explanations for the similar catalytic behaviour of cleaved and oxygen sputtered HOPG are:

- 1- The sputtering is unable to produce the (active) oxygenated functional groups. It may not be able to create surface functionality at all, or it may have been able to create some inactive types of functional groups. In this case the observed activity for cleaved and oxygen sputtered HOPG should result from the carbon deposits which are created on the surface at the beginning of the reaction.
- 2- Some (active) surface oxygen complexes may be created on the surface by oxygen-sputtering, but these active centres are covered at the very beginning of the reaction by a closed layer of carbon deposits. This would happen quickly at a time much less than the response time of our experimental system. In this case, we would not be able to see the (initial) higher activity of oxygen-sputtered HOPG, but again the steady state activity of carbon deposits would be observed.

The observed activity of the HOPG samples looks very low in terms of percentage yield of styrene. The calculated reaction rate of about 1×10^{14} molecules/s \cdot 1.cm $^{-2}$ reflects the actual rather high activity of this material more clearly. It confirms the ability of HOPG to be used as a model catalyst for other carbon materials in ODH reactions.

In the post-reaction investigations, temperature programmed spectroscopy techniques have shown the surface deposits to be composed mainly of carbon and oxygen. The absence of hydrogen or water desorption peaks indicates the absence of hydrocarbons in the depositions. This supports the idea that the carbon depositions on the surface in our experiments are composed mainly of condensed aromatic rings. No RedOx behaviour of the carbon deposits could be observed.

SEM and AFM images have shown that the cleaved HOPG surface is smooth before and after reaction. This can be understood by the building of uniform film of carbon deposits during reaction. However, the sputtered surface was found to be rough before and after reaction. This is probably a consequence of rapid building of carbon deposits in form of hills over active centres on the sputtered surface, this will ,in turn, block these active centres and increase the roughness of the surface.