

# ROLE OF DEFECTS IN CARBON MATERIALS DURING METAL-FREE FORMIC ACID DEHYDROGENATION

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Carbon-based catalysis is attracting a lot of attention because of its sustainability. Moreover, carbon as a catalyst allows a large variation in the structure because it can be easily tuned. Intrinsic topological defect (i.e. vacancies and non-hexagonal rings derived from lattice reconstruction) can strongly influence the activity in functionalised carbon materials for oxygen reduction reactions<sup>[1]</sup>. Since the influence of topological defects in liquid phase catalysis is not widely reported in literature, we decided to focus the attention on the effect of them in formic acid decomposition using graphene as model catalytic material. We decided to use graphene due to its ability to reconstruct forming non hexagonal rings<sup>[2]</sup>.

Formic acid (FA) was selected as substrate because it is the most suitable chemical for the production of H<sub>2</sub>. FA, in fact, is a non-toxic compound obtained from catalytic conversion of biomass and it possesses a high hydrogen content (4.4 wt%). FA can be easily decomposed into CO<sub>2</sub> and H<sub>2</sub> (the desired reaction) or into CO and H<sub>2</sub>O. The formation of carbon monoxide is detrimental for the catalysts because of its affinity with metals. The selective decomposition of formic acid can act as an elegant way to store hydrogen and recycling CO<sub>2</sub> to formic acid again<sup>[3]</sup>.

Here we propose a study on different surfaces, from pristine to defective graphene carrying out a systematic investigation using formic acid as a probe molecule. Different metal-free catalysts based on graphitic structures (pristine graphene, graphene oxide, PS carbon nanofibers and LHT carbon) were experimentally tested and their structures were analyzed by XPS and Raman spectroscopy. We found a correlation between the FA conversion and the number of defects presented in the catalysts. In particular, the FA decomposition increases by increasing the defectiveness of the material. This result was confirmed by both XPS and Raman techniques. In order to understand the role of the different types of defects, we investigated the decomposition of formic acid using the DFT models of pristine graphene and different defective graphene surfaces. We demonstrated that the activity is mainly due to the single vacancy defect because it is the only system able to decompose formic acid to gaseous molecules. Two different pathways were found but, in both cases, we obtained the saturation of the active site because of CO and atomic hydrogen irreversible adsorption. Different types of oxygen functionalities were investigated, but they did not show any activity in the adsorption of FA, confirming the experimental results, where no direct correlation between the oxygen groups and the catalytic behavior was observed. When the vacancies are completely saturated, the catalyst deactivates, explaining the experimental observations after 5 minutes of reaction<sup>[4]</sup>.

## References

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