Quantum Chemical Modeling of the Molecular Processes in the Carbon-Catalyzed Oxidation of Benzene Yielding Phenol

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The catalytic oxidation of organic species is a class of reactions of eminent importance for the chemical industry. Traditionally, such reactions are performed over metal oxide based catalysts. However, it has been demonstrated recently, among others at the example of the direct oxidation of benzene[1,2], that graphene-type carbon structures feature promising catalytic features.

A selectivity of 99% at a conversion rate of 18.5% has already been achieved for the oxidation of benzene with H_2O_2 to yield phenol. However, the current knowledge of the mechanistic details of this process is still limited. We report a computational study using periodic-DFT calculations to explore the mechanistic aspects of this reaction. We have started our study with the evaluation of the possible reactions using a pristine graphene surface to model the catalyst. It could be demonstrated that the activation of the benzene C-H bond, ultimately leading to the oxidation of benzene, is kinetically and thermodynamically hindered on pristine graphene surfaces. At variance, the activation of benzene at surface oxygen sites is more accessible. However, the activation of H_2O_2 to yield the oxygen groups on the surface is, though being a thermodynamically neutral process, hindered due to its high activation barrier, indicating that the pristine surface is essentially inactive for the benzene oxidation reaction. First results have shown that the activation of H_2O_2 yielding activated oxygen groups may occur at the edge sites of graphene. This finding is consistent with the experimental literature which proposes that the catalytic activity originates from the edge sites of the graphene-like structures.

References:

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