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Modelling the reactivity of carbon materials: oxidation and bromination

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Functionalized carbon materials (CMs) are promising starting point to create selective sorbents and solid catalysts. Among their advantages are a high specific surface area and the possibility of imparting specific chemical groups that enable changing the hydrophobic-hydrophilic and acid-base properties of the surface. The aim of this work was to evaluate the reactivity of CMs in model reactions, namely, in the bromination and oxidation reactions. For this purpose, the active centers of carbons were simulated with the density functional theory methods. It was shown that in all of nine proposed models represent localized double bonds that are active centers of the surface. With an increase in the size of the carbon models, the edge double C=C bond becomes shorter, this increases the bond order and in such case, the affinity for the addition reactions becomes significant. The symmetry of models, the defects of the structure, vacancies of carbon atoms do not effect on the presence of the edge double C=C bond. We calculated the heat of formation of products of the interaction of active centers of the different carbon models with bromine and hydrogen peroxide. At these processes, the impact of neighboring substituents, functional oxygen-containing groups, was assessed. The calculation showed that the bromine molecules attacked the edge localized double C=C bond (H = –33 kJ/mol), which is more favorable than substituting of hydrogen with bromine (H = –26 kJ/mol). The bromination does not change the neighboring functional groups. The oxidation reaction, as compared to the bromination, is the more advantageous process. Grafting of phenolic groups is characterized by a very significant heat of the product formation. The formation of phenolic groups can also be imagined by the mechanism that will account the hydrolysis of bromine. This speculation is in a good accordance with the results of the test study. Thus, we investigated the nature and properties of surface carbon active centers, which will help to understand the carbon reactivity and also energetic of the reaction that passes through the centers of the carbon surface.