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Conclusions

Presented here is an experimental study on the thermal desorption of polyaromatic hydrocarbons (PAHs), hydrogen peroxide (H_2O_2) and ethylbenzene ($C_6H_5C_2H_5$) from graphitic (highly oriented pyrolytic graphite) and porous carbon surfaces (single-wall carbon nanotubes, carbon nanofibers and colloidal graphite).

Thermal desorption experiments of four polyaromatic hydrocarbon molecules (benzene, naphthalene, coronene and ovalene) from the basal plane of graphite were performed in order to determine the graphitic interlayer cohesive energy. The determination of this cohesive energy is based on the topographic and electronic similarities between PAH molecules and a graphene sheet. Therefore, the interaction between PAH molecules and the graphene sheet gives a good approximation of the interlayer interactions in graphite. The binding energies of the PAH molecules on graphite were independently obtained by Falconer-Madix and Redhead's peak maximum method. They are found to be: 0.05 ± 0.08 (benzene), 0.85 ± 0.08 (naphthalene), 1.40 ± 0.11 (coronene) and 2.07 ± 0.11 eV (ovalene). This binding energy is found to have a linear dependence on the molecule's static-polarizability. Also, the binding energy is found to have zero-offset when extrapolated to zero polarizability. This linear scaling of the binding energy, and the vanishing of the binding energy at zero polarizability, confirms that the PAH-graphite system is in agreement with the united-atom model of adsorbate-substrate interactions. Therefore, it is concluded that the interaction between the PAH molecules and a graphite basal plane is dominated by van der Waals interactions. The experimentally obtained PAH binding energies were used to derive the contributions of individual carbon atoms, which in the limit of infinitely large PAHs, corresponds to the energy required to separate a single graphene sheet from its parent crystal. The individual

contributions are obtained using the MM3 pair potentials for carbon-hydrogen and carbon-carbon interactions. The resulting cleavage energy, $61 \pm 5\,\text{meV/atom}$, is significantly larger ($\sim 42\%$) than previously reported experimental values. The pre-exponential frequency factors for PAH desorption are found to be considerably larger than those from the desorbing smaller molecules. They are found to increase from $10^{15}\,\text{s}^{-1}$ for benzene to $10^{21}\,\text{s}^{-1}$ for ovalene. This increase is qualitatively attributed to the suppression of the vibrational degrees of freedom of the adsorbed PAH molecules.

The second part contains the oxidation of carbon nanofibers and colloidal graphite are using hydrogen peroxide. The thermal desorption spectra of oxygen adsorbed on to carbon nanofibers exhibits a single a broad desorption feature. Oxygen adsorbed on colloidal graphite surface, on the other hand, exhibits two different adsorbed phases having binding energies of $0.35 \pm 0.02\,\text{eV}$ and $1.81 \pm 0.11\,\text{eV}$. The broadening of desorption peaks on SWNT bundles is attributed to diffusion of the adsorbates within the inner void spaces. The broadening of desorption peaks on carbon nanofibers and colloidal graphite is attributed to the presence of inhomogeneities due to the high density of defect sites and reactive edge planes observed in these samples. By comparing the oxidation of polyaromatic hydrocarbons with peroxide obtained from classical organic chemistry, a reaction mechanism for the oxidation of carbon surfaces was proposed. This mechanism supports the Eley-Rideal kinetics. However this mechanism is more suitable to carbon nanofibers, because their exposed surface is characterized by only edge planes. On the other hand, the two widely separated distinct desorption features from colloidal graphite suggest that adsorption occurs at two energetically different sites, such as the basal and edge planes in colloidal graphite. The adsorption of oxygen and the subsequent surface migration suggests that reaction mechanism proceed through a Langmuir-Hinshelwood type of reaction mechanism. The thermal desorption of carbon monoxide and carbon dioxide from oxidized carbon surfaces was monitored to establish the types of carbon-oxygen surface functional groups that are present. The CO_2 and CO desorption spectra are characterized by complex features with major peaks below $700\,\text{K}$. A comparison with the decarbonylation and decarboxylation reactions in traditional organic chemistry, reveals that the oxidized carbon surfaces are predominantly occupied by acid and acid anhydride surface groups.

The final part of this work focuses on the catalytic properties of oxidized carbon surfaces, using the oxidative dehydrogenation of ethylbenzene as a model reaction. For this, the thermal desorption of ethylbenzene was carried out on the surfaces oxidized carbon nanofibers and colloidal graphite. Assuming a Langmuir-Hinshelwood reaction mechanism, the activation energy for the desorption and binding energy of ethylbenzene on oxidized carbon surfaces were determined. The energetics of ethylbenzene desorption from the oxidized carbon surfaces is found to be similar to that of the pristine carbon surfaces ($0.68 \pm 0.01\,\text{eV}$ on HOPG and $1.02 \pm 0.01\,\text{eV}$

on porous surface). The mechanism for the styrene formation is explained by extending the similar one found in classical organic chemistry reaction. This mechanism involves the reaction between a physisorbed styrene molecule with surface-functional group of the carbon surfaces. Using the instantaneous surface coverages of the educt (ethylbenzene) and the product (styrene), obtained from the integrated thermal desorption spectra, percentage conversion and selectivity are determined. It is observed that in general the catalytic properties of carbon nanofilaments are excellent compared to those of colloidal graphite. The percentage conversion of ethylbenzene was found to be $15\,\%$ at $200\,\mathrm{K}$ which increased to $25\,\%$ at $400\,\mathrm{K}$. The low conversion rate observed in our experiments when compared to the traditional ODH reaction, is attributed to the low residence time of the educt on the surface during a thermal desorption experiment. Carbon nanofilaments displayed a selectivity of $20\,\%$ at $200\,\mathrm{K}$ which increased to $93\,\%$ with increasing temperature to $400\,\mathrm{K}$. As these quantities are described in terms of surface concentrations, the thermal desorption experiment revealed that at a surface level, the oxidative dehydrogenation reaction has proceeded almost to completion.

Outlook

The desorption energies of PAHs reported here can serve as a benchmark for the future studies, and allows for better comparison to theoretical binding energies.

Experiments with hydrogen peroxides have indicated that carbon nanofibers and colloidal graphite can be oxidized at low temperatures. It also suggests that the oxidation reaction mechanism can be different depending on the availability of highly reactive sites. However, further experiments are required to fully characterize the various functional groups, in particular those which decompose at higher temperatures. It is also important to carry out similar decarbonylation and decarboxylation reactions with simpler molecules in similar conditions (UHV and low temperature) in order to conclusively establish the identity of the surface groups. The ODH reaction of ethylbenzene has demonstrated that oxidized carbon surfaces are good catalysts, exhibiting a very high selectivity at relatively low temperatures. However, further studies need to be conducted to understand the reasons behind the low conversion of ethylbenzene and to rectify it. Also, additional experiments are required in order to characterize the various reaction intermediates.