

Kurzfassung

Eine experimentelle Untersuchung der thermischen Desorption von ausgewählten Molekülen (polyaromatische Kohlenwasserstoffe (PAH), Wasserstoffperoxid und Ethylbenzol) von vier verschiedenen Kohlenstoff-Oberflächen (hoch orientiertes pyrolytisches Graphit, einwandige Kohlenstoff-Nanoröhren, Kohlenstoff-Nanofasern und kolloidales Graphit) wird in der vorliegenden Arbeit vorgestellt. Neben der Messung der kohäsiven Lagen-Bindungsenergie im Graphit ist ein Verständnis der Oxidation von porösen Kohlenstoff-Oberflächen und der katalytischen Eigenschaften dieser Oberflächen für die oxidative Dehydrierung (ODH) von Ethylbenzol von Interesse.

Durch die thermische Desorption der vier polyaromatischen Kohlenwasserstoffe (Benzol, Naphthalen, Coronen, Ovalen) von der basalen Graphitoberfläche werden deren Aktivierungsenergien für die Desorption, präexponentielle Frequenzfaktoren und Desorptionsordnungen ermittelt. Es zeigt sich, dass die Bindung zwischen den PAH und Graphit auf einer schwachen Van der Waals-Wechselwirkung (Physisorption) beruht. Die präexponentiellen Frequenzfaktoren der PAH sind deutlich größer im Vergleich zu denen einfacherer bzw. kleinerer Moleküle auf Graphit. Dies ist durch den Vergleich der statistischen Zustandsumme, im Speziellen die Betrachtung aller zulässigen Schwingungen, der PAH-Moleküle im adsorbierten („eingefrorenen“) Zustand und im so genannten Übergangszustand (während der Desorption) qualitativ verständlich. PAH sind flächige Moleküle, die als kleine Stücke einer Graphitschicht aufgefasst werden. Aus den Bindungsenergien der PAH an Graphit lässt sich, durch die Optimierung der Kohlenstoff-Kohlenstoff- bzw. Kohlenstoff-Wasserstoff Wechselwirkungspotentiale in einer Molekularmechanik-Berechnung (MM3), die kohäsive Lagen-Bindungsenergie pro Kohlenstoff-Atom im Graphit zu 61 ± 5 meV berechnen.

Die Kohlenstoff-Nanofasern und das kolloidale Graphit wurden mit Wasserstoffperoxid oxidiert. Irreversible Veränderungen durch die Oxidation der Kohlenstoff-Oberflächen wurden durch thermische Desorption von Sauerstoff, Kohlenmonoxid und Kohlendioxid nachgewiesen. Zum Beispiel desorbiert molekularer Sauerstoff, der bei dieser Oxidation entsteht, bei deutlich höheren Temperaturen, die auf eine stärkere Bindung (Chemisorption) hinweisen, von oxidierten Kohlenstoff-Oberflächen als von einwandigen Kohlenstoff-Nanoröhren. Die Oberflächen-Sauerstoff-Funktionalisierungen, die durch die Oxidation entstehen,

sind überwiegend sauer, wie die Temperaturen, bei denen die Decarboxylierung und Decarboxylierung der Kohlenstoff-Oberflächen auftritt, zeigen.

Die Bindungsenergien, Frequenzfaktoren und Desorptionsordnungen von Ethylbenzol auf Graphit, einwandigen Kohlenstoff-Nanoröhren, Kohlenstoff-Nanofasern und kolloidalem Graphit wurden mit Hilfe der thermischen Desorption ermittelt. Ethylbenzol ist auf allen vier Kohlenstoff-Oberflächen durch schwache Van der Waals-Kräfte gebunden. Die katalytische Aktivität von oxidierten Kohlenstoff-Nanofaser- und kolloidalen Graphit-Oberflächen im Hinblick auf eine oxidative Dehydrierung wird ebenfalls durch thermische Desorption von Ethylbenzol von diesen Oberflächen untersucht. Unter Annahme eines Langmuir-Hinshelwood-Reaktionsmechanismus werden die Bindungsenergien und präexponentiellen Faktoren für den Ausgangsstoff (Ethylbenzol) und das Reaktionsprodukt (Styrol) bestimmt. Diese liegen sehr dicht bei den Werten von nicht oxidierten Oberflächen. Entsprechend den vorherrschenden tiefen Reaktionstemperaturen und hohen Desorptionsraten ist der prozentuale Umsatz von Ethylbenzol in Styrol sehr gering auf den oxidierten Kohlenstoff-Oberflächen im Vergleich zu Eisenoxid-Katalysatoren, die typischerweise für die ODH - Reaktion verwendet werden. Jedoch weist die hohe Empfindlichkeit der Kohlenstoff-Oberflächen für die Styrol-Bildung darauf hin, dass die OHD-Reaktion hier nahezu vollständig abläuft.

Abstract

Presented is an experimental study of thermal desorption of polyaromatic hydrocarbons (PAHs), hydrogen peroxide (H_2O_2) and ethylbenzene ($\text{C}_6\text{H}_5\text{C}_2\text{H}_5$) from four different graphitic carbon surfaces: highly oriented pyrolytic graphite, single-wall carbon nanotubes, carbon nanofibers and colloidal graphite. These thermal desorption experiments are carried out with the objective of understanding three different aspects about carbon surfaces: First, to determine the interlayer cohesive energy of graphite; second, to study the oxidation of porous carbon surfaces; and finally to determine the catalytic performance of carbon surfaces for oxidative dehydrogenation (ODH) of ethylbenzene.

Thermal desorption of the four polyaromatic hydrocarbon molecules: benzene, naphthalene, coronene and ovalene, from the basal planes of graphite are used to obtain their activation energies for desorption, pre-exponential factors and orders of desorption. From the magnitude of the binding energies of the PAHs, and also from the zero-offset in the linear dependence of the PAH binding energies on respective molecular static-polarizability, it is concluded that physisorption is the interaction between PAHs and graphite surface (van der Waals interaction). The pre-exponential frequency factors of desorption are found to be considerably larger in comparison to those of smaller molecules, which qualitatively is concluded to arise from large differences in the vibrational partition functions of the PAH molecules in the adsorbed and transition states. Using the binding energies of the PAH molecules on graphite, the binding energy contribution arising from a single carbon atom of a graphene sheet is derived. This is done by optimizing the PAH binding energies using the carbon-carbon and carbon-hydrogen interactions potentials obtained from molecular mechanics (MM3) force-field calculations. The resulting interlayer cohesive energy (61 ± 5 meV/atom) is found to be 42% larger than the previously reported value.

Oxidation of the carbon nanofibers and colloidal graphite is performed using hydrogen peroxide. The thermal desorption of oxygen, carbon monoxide and carbon dioxide from these oxidized carbon surfaces shows that these surfaces undergo an irreversible change upon exposure to the oxidizing agent. The binding energy of oxygen on these carbon surfaces is found to be remarkably large when compared to reported oxygen binding energies on single-wall carbon nanotubes and falls into the range of chemisorption binding energies. From the temperatures corresponding to

decarbonylation and decarboxylation of the oxidized carbon surfaces, the surface-oxygen functionalities are found to be predominantly acidic, such as carboxylic acid and acid-anhydride functionalities.

Similarly, using thermal desorption of ethylbenzene from the surfaces of graphite, single-wall carbon nanotubes, carbon nanofibers and colloidal graphite, the corresponding activation energies of desorption and pre-exponential frequency factors are also obtained. As with the PAHs, it is concluded that these molecules are held on the surface by van der Waals interaction, due to the magnitude of their binding energies. Thermal desorption of ethylbenzene from the surfaces of oxidized carbon nanofibers and colloidal graphite was performed to gain a better understanding of oxidative dehydrogenation on carbon surfaces. Invoking the Langmuir-Hinshelwood mechanism for the oxidative dehydrogenation, the binding energies and pre-exponential factors of the reactant (ethylbenzene) and the product (styrene) are calculated. They are found to be very close to those of a pristine carbon surface. Owing to low reaction temperatures, and also due to small contact times, the percentage conversion of ethylbenzene on the two above carbon surfaces was found to be much lower than observed in the traditional iron-oxide catalyzed ODH reactions. However, a high selectivity to form styrene indicates that the ODH reaction has proceeded to near-completion on porous carbon surfaces.

To sum up, we obtained the interlayer cohesive energy of graphite using the thermal desorption from a well-defined model system. We have shown that colloidal graphite and carbon nanofibers are prone to oxidation at low temperatures if a powerful oxidizing agent is used. These oxidized carbon surfaces serve as high-selectivity catalysts for oxidative dehydrogenation of ethylbenzene.

Publications

The research presented in thesis has resulted in the following publications and presentation at conferences:

- Renju Zacharia, Hendrik Ulbricht and Tobias Hertel, “Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons,” *Physical Review B*, **69**, (2004) 155406.
- Hendrik Ulbricht, Renju Zacharia, Nesibe Cindir, Anne-Isabelle Henry, Axel Hagen, Gunnar Moose and Tobias Hertel, “Interactions of gases with graphite from thermal desorption spectroscopy,” *to be submitted*.
- Renju Zacharia, Hendrik Ulbricht and Tobias Hertel, “Thermal desorption spectroscopy of polyaromatic hydrocarbons from graphite,” presented at the Deutsche Physikalische Gesellschaft (DPG) Spring Meeting, Dresden, Germany (2003).

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