"All truths are easy to understand once they are discovered; the point is to discover them."

Galileo Galilei (1564-1642)

1 Introduction

Carbon is the single element that offers challenges to researchers in diverse fields: from physics and chemistry to material science and nuclear research. For chemists, it is an ideal element, because, by obeying a few elementary valency rules, they can make structures of great complexities out of it: from fullerenes and quasi one-dimensional nanotubes to two-dimensional graphite and three-dimensional diamond. These polymorphic forms of carbon exhibit an exceptional range of properties, such as the highest room temperature thermal conductivity, the greatest Young's modulus and the hardest natural material. A vast majority of novel carbon materials (carbon nanotubes, carbon nanofibers etc.) are characterized by sp^2 hybridized carbon atoms, and therefore are related to the structure of graphite. The goal of the research presented in this thesis is to understand the interlayer binding and catalytic properties of these sp^2 hybridized carbon surfaces.

The work presented in this thesis can be broadly split into two parts: the first part is an experimental characterization of the interlayer binding energy in graphite is presented. The second part is a study of the oxidation, and catalytic properties of various carbon surfaces. The graphitic interlayer binding energy — a measure of the strength that holds the graphene layers together — is the crucial parameter that controls the tribological properties (lubrication and frictional properties) of graphite and many graphitic composite materials. The precise knowledge of this interlayer cohesive energy is required to tailor and interpret the properties of graphite intercalation compounds (GIC), which can be found as anode materials in Li-ion batteries.

The interlayer binding energy of graphite and similar layered materials is dominated by weak, long-range van der Waals interactions. Due to this weak interaction and the extremely anisotropic bonding in graphite, the determination of the inter-

layer binding energy has remained a true challenge to both theoreticians and experimentalists. Theoretical calculation of this binding energy using density functional theory (DFT), today's standard tool for electronic structure calculations, gives inaccurate results. Thus, the application of DFT to graphite is considered an acid test for various approximation within the density function formalism when applied to van der Waals bonded systems. The experimental determination of this interlayer cohesive energy on the other hand, has been limited to two values: one obtained from a heat of wetting experiment, and the other from an experiment involving the deflation of multi-wall carbon nanotubes [Benedict et al., 1998; Girifalco and Lad, 1956]. The sample dependence of the results and other statistical uncertainties in these experiments are not known and hence a comparison with theory is difficult. Clearly, additional experimental measurements of the interlayer binding energy is necessary not only to make a comparison with theoretical results but also to put the previous experimental values on a solid footing.

The experimental characterization of the graphitic interlayer cohesive energy, is performed using the thermal desorption of polyaromatic hydrocarbon (PAH) molecules — a model system — from graphitic basal planes, and will be presented in the first part of this thesis. Key questions that arise in studying the thermal desorption of PAH molecules from a graphite surfaces are:

- Can the interaction between PAH molecules and a graphite surface be described in terms of van der Waals forces? Are van der Waals interactions responsible for the dispersion of π-electrons perpendicular to graphene sheets?
- What is the magnitude of the interlayer cohesive energy of graphite?
- How does the graphite vdW interaction potential compare to vdW potentials used in modeling carbon-carbon interactions in other systems.
- How does the binding energy scale with number of carbon atoms in PAH? The united-atom model of adsorbate-surface interaction predicts a zero-offset linear dependence of hydrocarbon binding energy on the number of carbon atoms. However, experimental results have indicated an anomalous non-zero linear scaling of binding energy; the origin of which is yet unresolved [Lei et al., 2004].

In the second part of this thesis, studies on the oxidation of porous carbon surfaces (carbon nanofibers and colloidal graphite) and the application of these oxidized carbon surfaces as heterogeneous catalysts are presented. The reaction of molecular oxygen with carbon surfaces is one of the simplest reactions involving elemental carbon, and it is also the most important reaction with regard to key diverse technological applications. This reaction has long been studied, however, in many of the previous experiments, the carbon surfaces are vaguely described as "coke" or "soot".

This description is a source of uncertainty due to the extremely high structural diversity exhibited by different forms of carbon. The aim of this study is to explore the oxidation of colloidal graphite and carbon nanofibers — two carbon surfaces that are characterized by sp^2 hybridized carbon atoms — when they are exposed to an oxidizing agent (hydrogen peroxide) at low temperatures (77 K). This thesis will address the mechanism of these oxidation reactions, and the formation and stability of surface functional groups that are created by the oxidation.

The final part of this thesis presents a study on the catalytic properties of oxidized carbon surfaces. The model reaction for this process is the oxidative dehydrogenation (ODH) of ethylbenzene (C_8H_{10}) to styrene (C_8H_8). The catalytic conversion of ethylbenzene into styrene is one of the top ten industrial processes [Kochloefl, 1997]. It is presently conducted using a dehydrogenation (DH) reaction, which is a energy consuming and less efficient method:

$$C_8H_{10} \underset{+H_2O\,,-H_2}{\overset{K-\ Fe_2O_3}{\rightleftharpoons}} C_8H_6, \quad \Delta H^0_{298} = +117.5\,\mathrm{kJ\,mol^{-1}}.$$

Recent studies of the oxidative dehydrogenation suggested that an ODH reaction using carbon is a possible alternative for styrene synthesis. The conversion can be achieved at lower temperatures and also yields a higher efficiency [Maximova, 2002]. The mechanism of this ODH conversion is still under debate. The precise role of any oxygen functional groups on the surface is also unknown. The oxidative dehydrogenation of ethylbenzene, as presented in the final part of this thesis, is investigated using an unconventional approach: thermal desorption spectroscopy of the educt (ethylbenzene) and product (styrene). The advantage of this approach is that surface concentrations of the educt and the product can be directly obtained from the thermal desorption spectrum. Hence, the conversion and the selectivity of the ODH reaction can be described using a thermal desorption experiment because it will reflect the true contribution from the adsorbed educt and products. In course of this study, I intend to address following three key issues related to the ODH reaction on a carbon surface:

- What is the dominant interaction between ethylbenzene and an oxidized carbon surface? Does the oxidation of carbon surfaces alter their interaction with ethylbenzene? The activation energy of desorption from the surface is a crucial parameter upon which the residence time of the adsorbate on the surface depends, and therefore it is crucial parameter for the heterogeneous catalytic surface reaction's efficiency.

- Is there a correlation between the ODH reaction on the surface and the traditional organic chemistry conversion for the proposed reaction schemes?

- How efficient is the oxidized carbon surface for the ethylbenzene ODH reaction? What is the percentage conversion and the selectivity of this reaction?

The thesis is organized as follows:

Chapter 2 gives a conceptual background to the phenomena of adsorption and desorption. A brief overview of adsorption in the context of heterogeneous catalysis is also provided.

Chapter 3 provides the details of experimental techniques adopted, the preparation of the sample surface, and methods for analyzing the experimental data.

Chapter 4 covers the experimental determination of the interlayer cohesive energy. Here thermal desorption spectra of PAH molecules from the basal plane of graphite are used to obtain the relationship between the binding energies and the number of carbon atoms. Using this result, the binding energy contribution of single carbon atom is obtained.

Chapter 5 deals with the oxidation of colloidal graphite and carbon nanofilaments by hydrogen peroxide. The carbon-oxygen surface functional groups and their stability are discussed. By comparing the results to a reaction of hydrogen peroxide with polyaromatic hydrocarbons, a possible reaction is proposed.

Chapter 6 presents the oxidative dehydrogenation of ethylbenzene on oxidized carbon surfaces. A mechanism for the ODH reaction is discussed by comparing the reactions to those found in classical organic chemistry. Using the surface concentrations of ethylbenzene and styrene, the conversion and selectivity of the ODH reaction are determined.

Chapter 7 provides the summary and also presents open questions.