CARBON NANOMATERIALS for GAS ADSORPTION
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The increasing interest in new technological solutions for gas storage, requiring the development of novel solid state media, led to the benchmarking of nanostructured carbon allotropes as one of the ongoing strategic research areas in science and technology.

The variety of carbon bonding arrangements is at the root of the complexity and diversity of structures and configurations exhibited by new carbon nanomaterials.

In the last few years there was an upsurge of papers and heated discussions about these undoubtedly fascinating few-dimensional entities that are expected to play a fundamental role in providing new routes for gas adsorption and storage.

This book was conceptualized to provide, on the one hand, an up-to-date look at ongoing experimental and theoretical activities in the rapidly progressing and evolving field of carbon science and technology and, on the other, a thorough critical investigation to clear the prevalent misunderstandings and errors. Its purpose is to contribute toward paving the way for current and future development of gas interactions with carbon nanomaterials.

Chapter 1 discusses major technological issues for the quantitative determination of gas sorption in carbon nanomaterials. The current techniques used to investigate the sorption properties of nanostructured and nanoporous carbons are described, with an emphasis on both experimental methodologies and potential sources of error in sorption measurements. This chapter raises some general methodological questions that deserve careful consideration by researchers working in the field of gas storage, especially those involved in R&D activities for hydrogen storage.

Chapter 2 reviews the past and present situation of hydrogen adsorption by carbonaceous nanostructures. The nature of hydrogen interaction with carbonaceous nanomaterials is thoroughly investigated, and the various mechanisms playing a role in H adsorption processes are critically discussed. The adsorbent materials taken into account in this chapter encompass the whole range of carbon nanostructures, from fullerenes to nanotubes, and
their uptake properties are reconsidered using novel approaches to interpret the literature data published up to now. This contribution offers a stimulating glimpse of future directions in the field of hydrogen storage for fuel-cell-powdered vehicular applications.

Chapter 3 deals with the hydrogen storage properties of a specific class of carbon nanomaterials, the carbon aerogels. Preparation methodologies and structural characterizations of various carbon aerogels are discussed with reference to the sorption properties of these materials, which are regarded as the most promising candidates for hydrogen storage at cryogenic temperatures.

Chapter 4 describes the sorption properties of fullerenes, astralene, and nano-size activated carbons with respect to oxygen, hydrogen, and nitrogen. Astralene is a new nanomaterial, and it is characterized by a polyhedral multilayer fulleroid-type structure that manifests properties interesting also for some unthought-of applications. These fullerene-like structures are indeed proposed not only as adsorbent materials but also as photosensitizers for singlet oxygen generation realized during photodesorption from irradiated surfaces or carbon nanoshells. Possible applications are foreseen in the fields of laser technology (fabrication of a fullerene-oxygen-iodine laser) and medicine (treatments of biological solutions).

Chapter 5 reviews the adsorption properties of hydrogen on graphene. The effects of H adsorption on the electronic states of graphene are described and discussed in the frame of a theoretical modelling. This approach takes into account H-molecule dissociative adsorption on edge defects of graphene and the subsequent systems involving chemisorbed hydrogen states on graphene surfaces.

Chapter 6 reports the experiments performed on a variety of gaseous species in connection with a novel exciting class of sp$^3$-coordinated carbon structures, namely the ultradispersed detonation diamond (UDD), characterized by crystal sizes in the range of 3–6 nm. The main features of gas desorption from such materials are analyzed and discussed along with some technological aspects related to their surface chemistry. A very important issue is the use of UDD systems as synthetic analogues of meteoritic nanodiamonds in simulated cosmochemical experiments.

In Chapter 7 a general analytical model for describing the thermodynamic stability of carbon nanotubes in the presence of gas adsorbates is presented. The fundamental model parameters are of simple thermodynamic quantities such as cohesive energies,
adsorption energies, and strain energies. The model, parameterized for the cases of exohedral adsorption of H, O, N, and H$_2$O, allows for the description of different types of adsorption configurations and densities and includes the re-hybridization of C atoms in the vicinity of adsorption sites. Using this model, the stability of nanotubes in air is examined as a function of the relative humidity.

Chapter 8 delves into some of the most popular theoretical approaches pertaining to atomic simulations and related techniques of gas adsorption. It shows how \textit{ab initio} total energy calculations are essential in case of impurities, doping, chemisorption, and sensoring due to the inherent complexity of the samples and processes involved.

Last but not least, Chapter 9 reviews the fundamental properties of carbon nanotubes that govern their electronic structure and chemical reactivity, in terms of their effects on gas adsorption and sensing. Remarkable space is given to the structure, the chemical state and the post-synthesis treatments of the nanotubes to be used as sensing material with high sensitivity and chemical selectivity. The major technological issues for the fabrication of efficient gas sensors are analysed and discussed together with the challenges that must be addressed for integration of these carbon nanomaterials into efficient, robust and miniaturised sensors.

We thank the leaders of the groups who collaborated with us on the preparation of this book for their patience, advice, and help. We are also grateful to all their co-authors and other collaborators for taking part in these relevant research activities.

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