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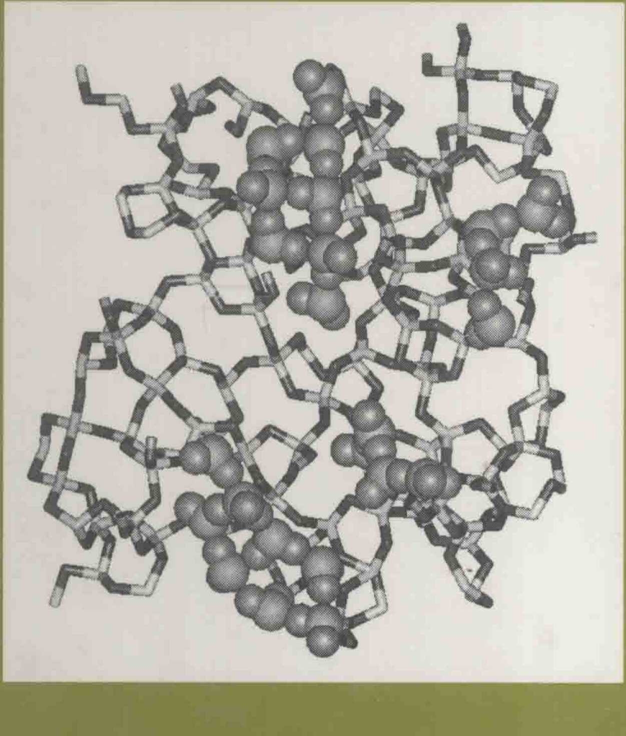

edited by
Eugène Papirer

ADSORPTION ON SILICA SURFACES

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Eugène Papirer

Institut de Chimie des Surfaces et Interfaces
Mulhouse, France

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Preface

Silicon is the earth's most abundant element. Silicon dioxide, or silica, appears in the form of crystalline minerals (principally quartz), stones, etc. It is prepared industrially on a large scale in the form of a powder of small particle size and high surface area. Silica has numerous applications. For instance, quartz enters into the preparation of ceramics, whereas silica powder has many applications in our lives.

Silica belongs to the limited number of finely divided mineral oxides whose surface properties have been studied extensively for years. Monographs and specialized conferences are currently devoted to the study of silica.

It is quite difficult to describe in a single volume the vast amount of information available in the literature. For this volume, we chose to concentrate our efforts on a given subject—the study of adsorption on silica surfaces. Adsorption on silica is fundamental to important applications, as demonstrated by the invaluable behavior of silica as a support in chromatographic phases, catalysts, etc. More recently, silica has become an efficient additive or reinforcement agent for rubber used in the preparation of tires. Its presence decreases rolling resistance, thus saving gasoline and consequently reducing air pollution. The unique adsorption properties and reactivity of silica in part explain this peculiar behavior. This is just one timely example that demonstrates the necessity for further investigation for a better understanding of the surface and adsorption characteristics of silica.

The book gives, as an introduction, a historical overview and discussion of the state-of-the-art of silica research. The first chapters allow nonspecialists to update their knowledge of silica surface characteristics.

The topics discussed include: (1) the surface chemistry of silica essentially as related to the existence of hydroxyl or silanol groups, which differ in nature and topology, as revealed by modern high performing techniques such as IR and NMR spectroscopies; (2) morphology at the nanoscale and mesoscale, as estimated by quantitative image analysis and molecular computer modeling; (3) porosity as determined by thermogravimetry methods; (4) surface energy or physical interaction potential, as shown by inverse gas chromatography.

Silica is commonly exposed to water in the form of vapor or liquid and thus it is important to learn more about the state and special properties of adsorbed water molecules. Indeed, subsequent solute adsorption processes have to take into account the electrical properties of the silica–water interface and adsorbed water behavior.

After this general introduction to silica, adsorption on nonmodified and modified silica surfaces becomes the major concern of the book. Adsorption from the gas phase, currently widely described in the literature, is in this book discussed in relation to ion-bombarded silica samples.

The nature of the adsorption medium, either water or organic liquids, strongly influences the adsorption process. Moreover, *micromolecular adsorbents*, such as heavy metal cations and surfactants, need to be considered separately from *macromolecular* species, such as polyelectrolytes and polymers used for the stabilization of silica suspension–supported enzymes and natural macromolecules finding interesting applications in biology. All these situations are examined in the book.

One chapter focuses on adsorption from organic solutions, which is of particular significance, especially for liquid chromatography separation techniques. Adsorption processes determine the performance of modified silica used as a chromatographic support. For important practical applications such as the manufacturing of polymeric (silicone) materials containing silica, hot melts for adhesives, etc., the fundamental study of the adsorption from the melt deserves special attention, and two chapters are devoted to this aspect. Whereas adsorption on silica is beneficial for many applications, the manipulation and or inhaling of finely divided, high-surface-area silica particles may generate health problems of great concern, as discussed here.

Finally, examples are provided detailing timely studies. First, the preparation of mesoporous silica with controlled surface chemistry and subsequent adsorption characteristics is presented, and then the role of silica particles in phase transformation of water and heterogeneous nucleation processes in the atmosphere is addressed.

In summary, this book contains a wealth of information on adsorption that will be useful not only for newcomers in the field of silica science but also for those with a general interest in adsorption phenomena. I am convinced that much progress will be made in the near future, following the development of more exact theories and the appearance of more sophisticated analytical methods (e.g., nanomicroscopies) allowing scientists to examine adsorption at the molecular level along with powerful computer simulation. It will not be very long before another complementary volume on this subject is necessary.

I would like to thank all the contributors, who prepared excellent chapters. I also acknowledge the dynamism and constant support of the publishing team at Marcel Dekker, Inc.

Eugène Papirer

Contributors

Henri Balard Institut de Chimie des Surfaces et Interfaces, Mulhouse, France

A. Bogdan Department of Physics, University of Helsinki, Helsinki, Finland

Aleksander Bródka Institute of Physics, University of Silesia, Katowice, Poland

Gianfranco Cerofolini ST Microelectronics, Agrate, Italy

Jean-Pierre Cohen Addad Department of Physics, University Joseph Fourier, Grenoble, France

Vladimir Ya. Davydov Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow, Russia

Martial Deruelle Rhodia–Silicone, Rhodia, Saint Fons, France

Patricia M. Dove School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia

V. Ehwald Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, Germany

Gamal M. S. El Shafei Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

Glen E. Fryxell Department of Material Sciences, Battelle Pacific Northwest National Laboratory, Richland, Washington

Bice Fubini Department of Inorganic, Physico-Chemical, and Material Chemistry, University of Torino, Torino, Italy

Ian D. Gay Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada

Jacek Goworek Department of Adsorption and Planar Chromatography, Maria Curie Sklodowska University, Lublin, Poland

F. Grossmann Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, Germany

Hubert Hervet Laboratoire de Physique des Fluides Organisés, Collège de France, Paris, France

Jonathan P. Icenhower Applied Geology and Geochemistry, Battelle Pacific Northwest National Laboratory, Richland, Washington

Erwin Killmann Institut für Technische Chemie, Technische Universität München, Garching bei München, Germany

Marek Kosmulski Department of Electrochemistry, Technical University of Lublin, Lublin, Poland, and Department of Physical Chemistry, Abo Akademi, Abo, Finland

Dipika Kumar Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, Germany

Liliane Léger Laboratoire de Physique des Fluides Organisés, Collège de France, Paris, France

Jun Liu Department of Material Sciences, Battelle Pacific Northwest National Laboratory, Richland, Washington

L. Meda EniChem, Centro Ricerche di Novara, Novara, Italy

Barry A. Morrow Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada

Eugène Papirer Institut de Chimie des Surfaces et Interfaces, Mulhouse, France

Jacques Persello Université de Franche Comté—UFR Sciences et Techniques, Besançon, France

N. Re Department of Chemistry, University of Perugia, Perugia, Italy

P. Somasundaran Henry Krumb School of Mines, Columbia University, New York, New York

V. A. Tertykh Institute of Surface Chemistry, National Academy of Sciences, Kiev, Ukraine

Klaus Unger Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, Germany

Henri Van Damme* Centre de Recherche sur la Matière Divisée, CNRS, and Université d'Orléans, Orléans, France

Caroll Vergelati Rhône Poulenc Industrialisation, CR Carrières, Saint Fons, France

William E. Wallace U.S. National Institute for Occupational Safety and Health, Morgantown, West Virginia

V. V. Yanishpolskii Institute of Surface Chemistry, National Academy of Sciences, Kiev, Ukraine

L. Zhang Henry Krumb School of Mines, Columbia University, New York, New York

---

**Current affiliation*: Laboratoire de Physico-Chimie, Structurale et Macromoléculaire, Ecole Supérieure de Physique et Chimie Industrielles, Paris, France.

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Brief Historical Review and Current State-of-the-Art of Silica

KLAUS UNGER and DIPIKA KUMAR Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Mainz, Germany

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I. THE CLASSICAL PERIOD

Following the invention of silica sols and gels in the 1920s and the manufacture of pyrogenic silica in the 1940s, finely dispersed and porous silicas became a subject of intensive research and development during the period 1950 to 1970. A number of internationally reputed scientists from both academic and industrial backgrounds have made substantial contributions to this field, including R. K. Iler [1] (Wilmington, USA), H. Bergna [2] (Wilmington, USA), A. V. Kiselev and his school (Moscow, Russia), C. Okkerse (Vlaardingen, The Netherlands), D. Barby [3] (Warrington, UK), J. T. Fripiat (Orleans, France), B. A. Morrow (Ottawa, Canada), K. S. W. Sing (Fairfield, UK), and H. K. Ferch (Hanau, Germany), among others.

During this period the formation of colloidal silicas, pyrogenic silica and silica xerogels, and precipitated silicas was studied in great depth with the aim of manufacturing products of technical importance with reproducible properties. These materials have found widespread application as fillers, lubricants, and adsorbents. The annual production amounts to about one million metric tons.

Comprehensive studies were also undertaken to characterize the silica surface in order to assess its adsorption behavior and its chemical reactivity. This led to a family of silica-based derivatives with controlled surface functionalities ranging from hydrophobic to polar surface characteristics.

II. MICROPARTICULATE POROUS SILICAS FOR CHROMATOGRAPHIC SEPARATIONS

The aforementioned achievements prepared the way for refined silica adsorbents which were chemically tailored and hence employed in chromatographic separations, mainly in the liquid phase [4]. Between the years 1970 and 1980, *n*-alkyl silanized mesoporous spherical silicas were developed, which created the basis for the advancement of so-called reverse-phase high-performance liquid chromatography (HPLC) [5–7]. This separation method is currently widely employed for the high-resolution separation of complex mixtures in the chemical and pharmaceutical industries, as well as environmental, food, and toxicological analysis. The main factor contributing to its success was the development of synthetic pathways in which both the pore structural properties and particle size distribution of the silica spheres were adjusted and controlled during the manufacturing process.

Apart from hydrophobic silanized silicas, other chemically bonded silicas have been synthesized with a specifically desired type, density, and topography of ligands [8]. These types of tailored adsorbents are not only employed for high-resolution analytical separation but also in process chromatography where they are used for the purification and isolation of value-added synthetic and natural products.

III. ADVANCES IN SOL–GEL SILICA CHEMISTRY

In the 1980s a renaissance in silica chemistry appeared which was rooted in the field of sol–gel chemistry [9]. During the course of this period, nanostructured silicas were synthesized as nanoparticles, monoliths, and coatings. These achievements were primarily accomplished due to the use of high-resolution spectroscopic and other related techniques, which enabled researchers to elucidate the mechanism of formation at nanoscale dimensions and, thus, to analyze the surface properties in greater detail than was previously done.

This field is still a major focus of research and development.

IV. MESOSTRUCTURED SILICA MATERIALS

Initiated by the advances of the template-driven synthesis of silica-rich, highly shape-selective zeolites, such as ZSM-5 in the 1970s, researchers of the Mobil Oil Corporation recently developed a new family of ordered mesoporous silica [10–12]. This materials breakthrough was accomplished by using surfactant liquid crystals (with long *n*-alkyl chains) as structure-directing agents to produce a new generation of silicate and aluminosilicate mesoporous molecular sieves (MMS) in the 1990s [3–