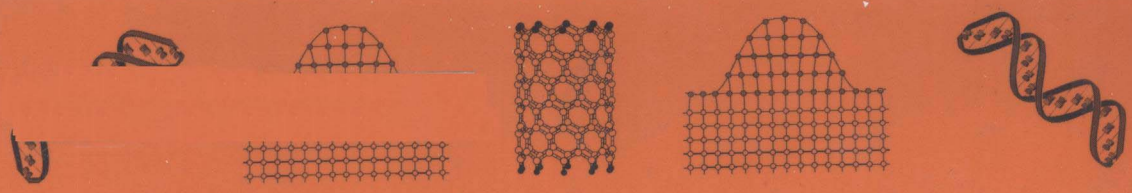

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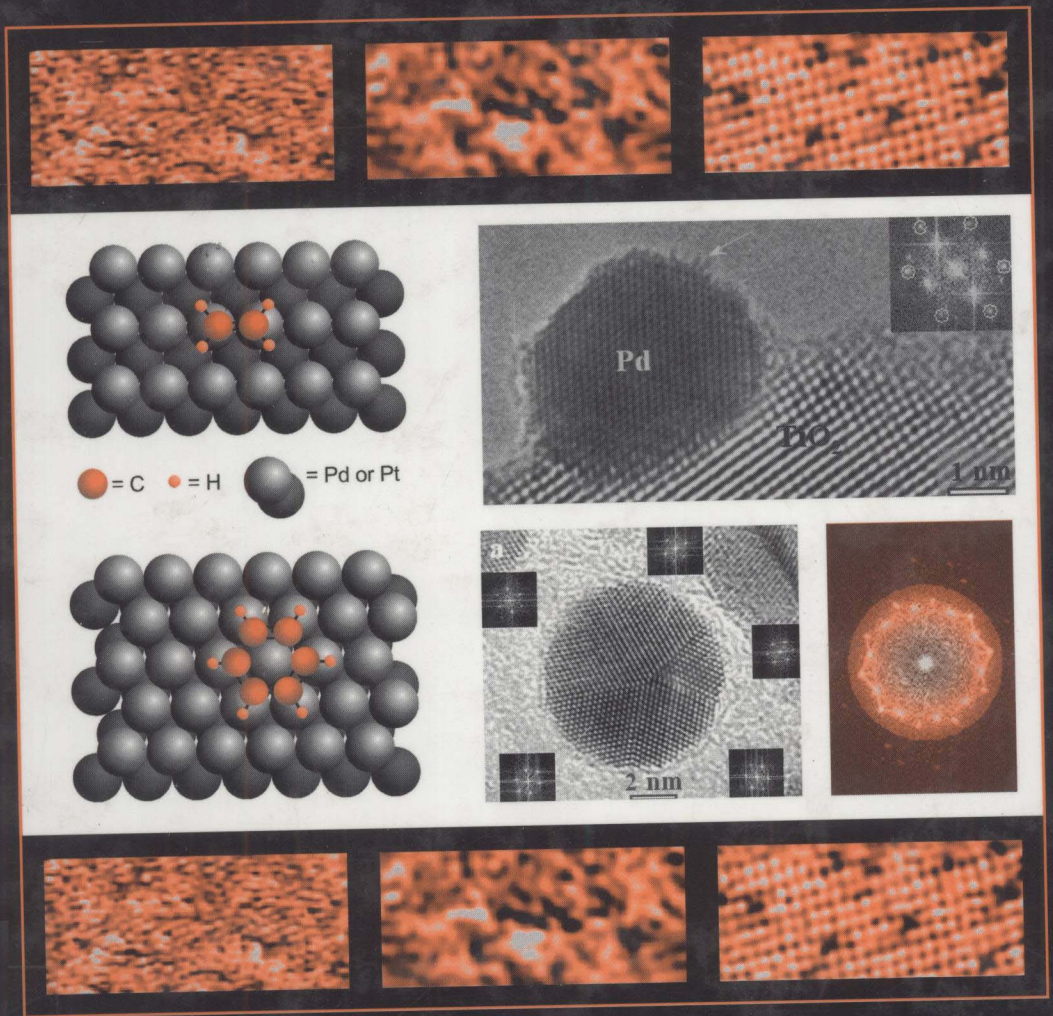
# *Nanotechnology in Catalysis*

*Volume 1*




Bing Zhou, Sophie Hermans,
and Gabor A. Somorjai

# Nanotechnology in Catalysis

*Volume 1*

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*Volume 1*

# Nanostructure Science and Technology

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# Preface

Catalysts, heterogeneous, homogeneous and enzyme, are usually nanoparticles. These are of vital for the functioning of the human body, for photosynthesis, and for producing fuels and chemicals in the petroleum and chemical industries. Interest in nanoscience and in nanotechnology in recent years focused attention on the opportunity to develop catalysts that exhibit 100% selectivity for a desired product, thus removing byproducts and eliminating waste. This type of selective process is often called green chemistry or green technology.

This book is mainly based on the first and second symposia on Nanotechnology in Catalysis which were held in spring 2001 at the ACS 221$^{st}$ National Meeting in San Diego, CA, and in fall 2002 at the ACS 224$^{th}$ National Meeting in Boston, MA, respectively. We also extended our invitation to those who did not attend the meetings to contribute chapters where we saw a need to round out the scope of the topic. All chapters were peer-reviewed prior to final acceptance. We believe that the additional chapters and the peer-review significantly improved the quality of the book.

In the summer of 2000 when we first proposed to organize a symposium on Nanotechnology in Catalysis to the ACS Secretariat of Catalysis and Surface Science (CATL), we received strong support from Dr. Nancy B. Jackson, then General Secretary of CATL. The symposium was enthusiastically received by the catalysis community. On the first day of the symposium, the conference room could not hold all the attendees. People were standing behind the last row of chairs or at the door to listen to the speakers.

Nanotechnology has become an important area globally. US Government spending on nanotechnology over the last two years is estimated at $2 billion. In The United States, legislation passed by the House of Representatives in April 2003 authorized $2.135 billion in federal research money for nanotechnology research and development over the next 3 years (Nano/Bio Convergence News, Vol.1, No.9, May 2003). The National Science Foundation (NSF) forecasts that the market value of nano products and services will reach $1 trillion by 2015 (NSF: Societal Implications of nanoscience and nanotechnology, March 2001). Similarly, the European Commission proposal for the 6th Framework Programme (2002 - 2006) contains a strong focus on nanotechnology. Out of a total proposed funding of 17.5 € billion, 1.3 € billion would be devoted to *"a priority thematic area of research on nanotechnology, knowledge-based materials and new industrial processes"* (source: www.cordis.lu, website of the European Commission).

Catalysis research and catalyst-based technologies have been at the heart of nanotechnology for many years. Nanotechnology is about manipulating and making materials at the atomic and molecular level. The development of supported noble metal catalysts in the 1950s aimed at reducing costs for large commercial applications resulted in catalysts with noble metal particle of sizes less than 10 nm, which by today's standard are nanomaterials. Zeolite catalysts, discovered in the late 1960s, are another example. By deliberate design and preparation of the catalyst structure at the atomic and molecular level, researchers at Mobil Oil Co. were able to synthesize zeolites such as ZSM-5, a nanostructured crystalline material with a 10-atom ring and pore size of 0.45-0.6 nm,

enabling the control of selectivity for petrochemical processes at a molecular level. Such nanomaterial catalysts revolutionized the petrochemical industry. Today, zeolite catalysts are used in processing over 7 billion barrels of petroleum and also many chemicals annually.

Research and development in the catalysis field have been in the nanometer scale since then. Recent developments of modern tools to characterize materials in nano or subnano scale provide insight for understanding and improving the existing catalysts, and clues for designing new nanomaterials for better catalysts.

The papers of this book reflect some of the frontier areas of nanoscience and nanotechnology to fabricate and characterize catalysts and carry out reaction studies to prove their selectivity and activity. This field of application of nanotechnology for the development of green catalysts is likely to grow rapidly during the next decade. This book hopes to contribute to the evolution of nanotechnology in this direction. The book is also a summary of updated advances and breakthroughs achieved worldwide by researchers in nanotechnology in the catalysis area. It is a difficult task to cover all aspects of such a dynamic research area. Also, there is no clear cut way to assign each contribution to well-defined topics. However, to facilitate comprehension of the advances in the field, the papers are organized into the following five sections.

Section I provides an overview of the fundamental understanding of catalysis and nanoscience. The evolution of the field of catalysis and its relation to nanoscience and nanotechnology are discussed. The authors describe the fabrication of 2- and 3-dimensional nanoparticle catalysts with controlled structures using electron beam and photo-lithography, providing the insight for possible catalyst fabrication in the 21$^{st}$ Century.

Section II focuses on nanoparticle and nanocluster catalysts. In this section, Chapters 2 to 6 describe the recent developments in synthesis and characterization of nanoparticle or nanocluster catalysts. Chapters 7 and 8 discuss the use of nanoparticle catalysts to grow carbon nanomaterials. The last part of this section (Chapters 9, 10 and 11) is devoted to noble metal nanoparticle materials as electrocatalysts, which are of vital importance for energy generation by fuel cells in the future.

Section III summarizes the recent advances in nanoporous materials as catalysts or catalytic supports. By controlling the structure of such materials at the atomic and molecular level, shape-selective and regio-specific catalysts are developed. The exceptional high selectivity of such nanoporous materials toward specific desired products has a potential to reduce or eliminate waste production. The chapters in this section provide clues for the new generation catalysts of the 21$^{st}$ Century, which may lead to green chemistry or green technology.

Section IV concentrates on the characterization and understanding of nanostructured catalysts and their properties by using modern tools and recently developed theories. Chapters 18 and 19 present how to use advanced and high-resolution electron microscopy to obtain detailed structural information at the nano-scale for catalyst development. New concepts and theories of characterization and understanding of heterogeneous catalysis at the nano-scale are discussed in Chapter 20 to 22.

Section V presents three examples of new nanomaterials as catalysts or supports. Researchers from the Dow Chemical Company explore the use of nanoscale dendrimers as hydroformylation catalysts. A study from Philip Morris examines the catalytic effect of nanoparticle iron oxide on carbon monoxide and biomass compounds. And finally, a

paper from the Dalian Institute of Chemical Physics in China discusses the use of graphitic nanofilaments as a superior catalyst support for ammonia synthesis.

In the spring of 2002 when we discussed the organization of the second symposium on Nanotechnology in Catalysis at the Catalysis Society of Metropolitan New York, both Professor Israel Wachs from Lehigh University and Dr. Gary McVicker from ExxonMobil noted that catalysis is an area that has moved one-step ahead of other areas in nanotechnology development. We are currently studying the catalyst materials at a subnanometer level. This provides an insight for how far we have advanced in the metered scale in catalysis. We have passed the nanometer level!

The first and second symposia on Nanotechnology in Catalysis were successful. We believe that their success and popularity are reflected in this book, which provides information on what has been done, and hopefully, an insight into what may happen in the future.

Gabor A. Somorjai
Bing Zhou
Sophie Hermans

# Acknowledegments

We are grateful to many people who have assisted and supported us in so many ways during the editing of this book. Without their involvement, the book would not have reached readers.

The suggestion from Dr. Kenneth Howell, Senior Editor at Kluwer Academic/Plenum Publishers, to publish the symposia on Nanotechnology in Catalysis as a book was a pleasant surprise to us. His initiation, dedication and persistence over last year helped us to overcome many obstacles and made the book project possible. His guidance on many detailed and time-consuming issues of the book was precise and led us through the difficult times. The vision of Kluwer Academic/Plenum Publishers in promoting science and technology is also acknowledged wholeheartedly.

The authors of each chapter in this book are acknowledged for their due diligence. Their contribution was essential to obtaining a high quality book. Many of the chapters have updated summaries of recent breakthroughs and developments made by the authors. We wish to thank all of them for their patience and persistence during the editorial process, which was a tedious and time-consuming task. They did an excellent job cooperating with the editors in a timely manner.

All chapters in the book have received extensive examination by a review committee. We are grateful to all the reviewers who contributed significantly in improving the quality of the book. Their contributions were not limited to critical comments on scientific content but also provided constructive and thoughtful suggestions. The discussions between authors and reviewers in some cases were intensive and intriguing. The review committee members are listed in the next pages. We highly appreciated their contributions and efforts to examine each chapter.

Our sincere and deep gratitude goes to many of our colleagues, associates and assistants for helping us in editing the book in time. In particular, Bing Zhou would like to thank his colleagues at Headwaters Technology Innovation Group, including Kelly Repoley, Rebecca Groenendaal, Patricia Livingstone, Jen Stone, Michael Elwell, Michael Rueter, Robert Stalzer, Rober Chang, and Sukesh Parasher. Sophie Hermans expresses her acknowledgements to Professor Michel Devillers for his support and patience throughout the realisation of this project, to Jacqueline Boniver for her secretarial assistance, and, most of all, to Benoît Poncin for his endless help and encouragement.

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# Nanotechnology in Catalysis

*Volume 1*

# Index