

Synthesis of Solid Catalysts

Edited by
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Preface

Solid catalysts are used in modern energy, chemical and environmental processes. Catalyst performance – activity, selectivity and stability – is largely determined by their preparation. In this respect, catalyst synthesis may be considered as one of the most influential ‘unit operations’ in industry. This book provides an introduction to basic concepts and research tools relevant to catalyst synthesis followed by a number of case studies. In this way it is an introduction to the field of catalyst synthesis for students and newcomers as well as a reference book for experienced scientists and practitioners. I hope that this book will stimulate the research field of catalyst synthesis and that it will support research and applications of solid catalysts by facilitating reliable and reproducible synthesis of materials.

For me it has been a privilege to work with so many colleagues in developing this book. I thank all of the lead authors as well as their co-authors for working with me on this project. It has been rewarding and I hope that we can continue to work together to foster and develop the field of catalyst synthesis.

I would like to thank Jos van Dillen and John Geus. They taught me as a graduate student at Utrecht University that catalyst synthesis is a research topic in its own right. For many years colleagues at the Shell Research Laboratories in Amsterdam provided a stimulating environment to synthesize and use solid catalysts. More recently at Utrecht University, staff, students and postdoctoral fellows have worked with me in the field of catalyst synthesis. Working with them has been a pleasure and is acknowledged.

Utrecht, December 2008

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Abbreviations

<i>AHM</i>	ammonium-hexa-molybdate
<i>BM</i>	base metal
<i>ccp</i>	cubic close packing
<i>CNF</i>	carbon nanofiber
<i>CNT</i>	carbon nanotube
<i>CT</i>	charge transfer
<i>CVD</i>	chemical vapor deposition
<i>D4R</i>	double four-ring
<i>D6R</i>	double six-ring
<i>DFG</i>	Deutsche Forschungsgemeinschaft
<i>DI</i>	dry impregnation
<i>DoE</i>	design of experiment
<i>DP</i>	deposition precipitation
<i>DTG</i>	differential thermal gravimetry
<i>EDF</i>	equilibrium deposition filtration
<i>EDTA</i>	ethylene diamine tetraacetic acid
<i>EDX</i>	energy-dispersive X-ray spectroscopy
<i>EPR</i>	electron paramagnetic resonance
<i>EXAFS</i>	extended X-ray absorption fine structure spectroscopy
<i>FCC</i>	fluid catalytic cracking
<i>FTIR</i>	Fourier transform infrared
<i>hcp</i>	hexagonal close packing
<i>HDMe</i>	hydrodemetallation
<i>HDN</i>	hydrodenitrogenation
<i>HDO</i>	hydrodeoxygenation
<i>HDS</i>	hydrodesulfurization
<i>HPA</i>	heteropolyacid
<i>IA</i>	ion adsorption
<i>ICI</i>	Imperial Chemical Industries
<i>iep</i>	isoelectric point
<i>IE</i>	ion exchange
<i>IL</i>	ionic liquid
<i>IR</i>	infrared

<i>IWI</i>	incipient wetness impregnation
<i>IZA</i>	International Zeolite Association
<i>MAS-NMR</i>	magic-angle sample spinning nuclear magnetic resonance
<i>MMA</i>	methyl methacrylate
<i>MOF</i>	metal organic framework
<i>MRI</i>	magnetic resonance imaging
<i>MTBE</i>	methyl tert-butylether
<i>(M)HC</i>	(mild) hydrocracking
<i>NMR</i>	nuclear magnetic resonance
<i>NM</i>	noble metal
<i>NTA</i>	nitrilo triacetic acid
<i>OHP</i>	outer Helmholtz plane
<i>Pc</i>	phthalocyanine
<i>PMO</i>	periodic mesoporous organosilica
<i>PTA</i>	platinum tetraammine
<i>PZC</i>	point of zero charge
<i>QMS</i>	quadrupole mass spectroscopy
<i>RDP</i>	reduction deposition precipitation
<i>RFC</i>	reactive frontal chromatography
<i>RPA</i>	revised physical adsorption
<i>RT</i>	room temperature
<i>SAPO</i>	SiAlPO ₄
<i>SCR</i>	selective catalytic reduction
<i>SDA</i>	structure-directing agent
<i>SEA</i>	strong electrostatic adsorption
<i>SRGO</i>	straight run gas oil
<i>STY</i>	space time yield
<i>3D</i>	three-dimensional
<i>TEA</i>	triethanolamine
<i>TEDDI</i>	tomographic energy-dispersive diffraction imaging
<i>TEM</i>	transmission electron microscope
<i>TEOS</i>	tetraethylorthosilicate
<i>TMA</i>	tetramethylammonium
<i>TMB</i>	trimethyl benzene
<i>TPA</i>	tetrapropylammonium
<i>TPD</i>	temperature-programmed desorption
<i>TPR</i>	temperature-programmed reduction
<i>2D</i>	two-dimensional
<i>USY</i>	ultrastable Y
<i>UV-VIS</i>	ultraviolet-visible spectroscopy
<i>VOC</i>	volatile organic compound
<i>XPS</i>	X-ray photoelectron spectroscopy
<i>XRD</i>	X-ray diffraction

PART I

Basic Principles and Tools

1

General Aspects

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1.1

Importance of Solid Catalysts

Catalysis is essential to modern energy conversion, chemicals manufacture, and environmental technology. From the start, oil refining and bulk chemicals manufacture have relied largely on the application of solid catalysts. In the meantime, in specialty and fine-chemicals production catalysis is used frequently too. According to current estimates about 85% of all chemical processes make use of catalysis, while all molecules in modern transportation fuels have been confronted with one or more solid catalysts.

Heterogeneous catalysts, or more specifically solid catalysts, dominate industrial catalysis. Of all industrial catalytic processes, 80% involves the use of solid catalysts with the remaining 20% for homogeneous catalysts (17%) and biocatalysts (3%). The world catalyst sales in 2004 amounted to 15 billion US\$/a, with 12 billion US\$/a for solid catalysts. The growth rate foreseen for catalyst sales amounts to about 5% per year (see Table 1.1) [1]. Although the catalyst sales comprise a significant market, the economic impact of catalysts is amplified by their use. The products (mainly fuels and chemicals) obtained by catalysts usage generate a margin that is a multiple of the catalysts costs. Data are scarce but indicative figures have been reported. For zeolite catalysis a paper by Naber and coworkers quotes figures on the costs of zeolites and their upgrading in heavy-oil cracking [2]. From their figures one can estimate the ratio of product margin divided by zeolite costs to be around 100 for fluid catalytic cracking as well as hydrocracking. If all energy and chemical industries are involved a ratio of 100–300 has been published [3] and it seems sufficient for the sake of argument that the total gross margin of the “catalysis industry” amounts to more than 100 times the catalyst sales, that is, more than 1500 billion US\$/a. The importance of research and manufacture of catalysts relates to this gross margin of their application.

Next to the economic importance we mention the environmental impact of catalysis. The amount of energy and raw materials needed for fuels and

Table 1.1 World catalyst demand and forecast (billion US\$/a) by application [1].

	2007	2010	2013	AAGR ^a
Refining	4.35	4.98	5.85	5.7
Petrochemicals	3.03	3.64	4.34	7.2
Polymers	3.24	3.75	4.30	5.4
Fine chemicals/other	1.47	1.59	1.70	2.5
Environmental	5.51	6.28	6.93	4.3
Total	17.6	20.2	23.1	~5

^a Average annual growth rate (%).

chemicals manufacture is much reduced by using catalysts. In fact today, many products could not be obtained without catalysis. Although sulfur removal from oil products started as extraction processes, today's low-sulfur diesel and gasoline could not be produced in an acceptable manner without hydrodesulfurization (HDS) catalysis. Exhaust catalysis has enabled the widespread use of cars, while selective catalytic reduction of nitrogen oxides has removed the brown plumes from power and chemical plants. In the future, the importance of catalysis will grow as raw materials for chemicals diversify and alternative energy sources and end use come into play. Building blocks in new energy chains, such as water electrolysis and fuel cells, also rely on solid catalysts.

1.2

Development of Solid Catalysts

In Table 1.2 selected solid catalysts are shown together with their main use. Bulk and supported catalysts as well as zeolite-based catalysts are listed. Many of the examples shown have been known for decades. However, a continuous and spectacular progress over the years is noted for many catalytic processes. We discuss two examples hereafter.

Based on the development of both catalysts and reactors [4, 5], the Fischer–Tropsch synthesis activity and selectivity of cobalt catalyst have increased as illustrated in Figure 1.1. The volume-based activity has increased by a factor of 10 going from 1940 at space time yield (STY) = 10 to 1990 at STY = 100, and another factor of 3 is expected to lead to STY = 300 by 2010. Most importantly, with increasing activity the catalysts displayed improved selectivities to higher hydrocarbons.

The second example, shown in Figure 1.2, involves the increase of the weight-based activity for HDS of NiMo catalysts over the years [6]. For quite a long period, say 1975–1995 the increase of activity has been modest, whereas a steep increase is apparent over the last decade. Low costs for HDS catalysts have been the predominating market factor for previous decades, whereas legislation for low-sulfur diesel has been a major driver lately. Market pull had

Table 1.2 Survey of selected catalysts with their main applications.

Catalyst	Applications
Ni/SiO ₂	Hydrogenation
K ₂ O/Al ₂ O ₃ /Fe	Ammonia synthesis
Ag/ α -Al ₂ O ₃	Epoxidation
CrO _x /SiO ₂	Polymerization
CoMoS ₂ / γ -Al ₂ O ₃	Hydrotreating
Co/SiO ₂	Fischer–Tropsch synthesis
Cu/ZnO/Al ₂ O ₃	Methanol synthesis
Zeolite Y composite	Catalytic cracking
Pt/Mordenite	Hydroisomerization of light alkanes
V ₂ O ₅ /TiO ₂	NO _x abatement
Pt/C	Hydrogenation; fuel cell

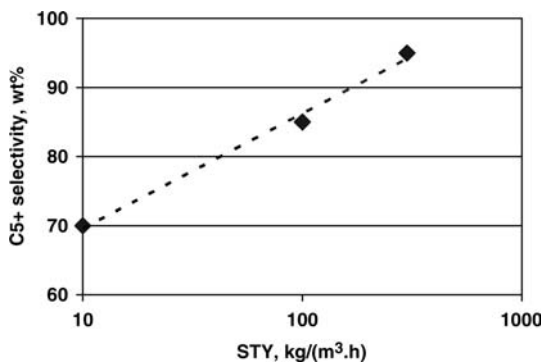


Figure 1.1 Development of cobalt-based Fischer–Tropsch synthesis in terms of both activity (STY = space time yield) and selectivity to hydrocarbons of five or more C-atoms. Data from 1940 to 2010 with data points from left to right at years 1940, 1990, and 2010, respectively.

quite an impact at all stages and it shows the great flexibility and potential of catalyst preparation to respond quickly.

One could easily put forward many other examples where catalyst preparation has been the basis for new and improved processes, such as methanol synthesis, ethene epoxidation, and acrylic acid production. However, for the topic of this book it is more important to discuss in which ways catalyst preparation has allowed these new developments.

1.3 Development of Solid Catalyst Synthesis

Depending on the application, macroscopic catalyst bodies differ in size and shape. For slurry and fluid-bed applications the size is in the range of

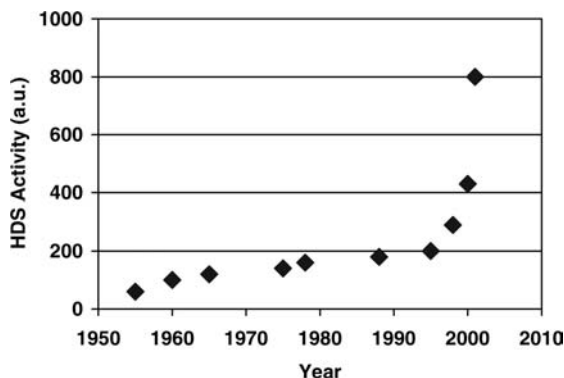


Figure 1.2 Development of hydrodesulfurization (HDS) catalyst activity over the years [6].

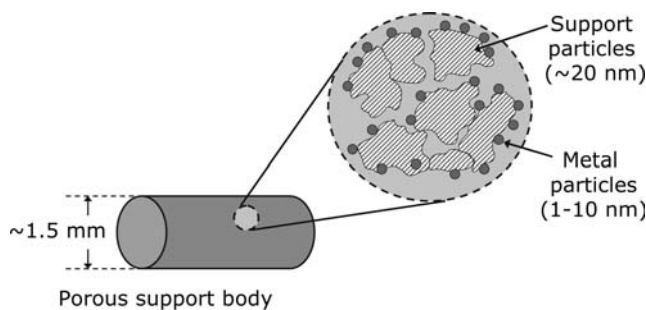


Figure 1.3 Structure at different length scales of catalyst extrudate.

tens of micrometers, whereas fixed-bed applications require millimeter-sized particles. Next to particles, monoliths are used with macroscopic sizes well beyond that of particles (Chapter 9). A typical structure for a cylindrically shaped catalyst body for fixed-bed application is shown in Figure 1.3. This figure also reveals the multiple length scales involved in solid catalysts. The microscopic scale involves the structure of the active sites, the mesoscopic scale the pore system and the sizes of support particles as well as the particles of the active phase. The macroscopic length scale involves the size and shape of the catalyst bodies. The importance of the microscopic scale goes without saying as it determines the intrinsic activity and selectivity of the catalyst. The mesoscopic length scale affects, amongst others, the intraparticle mass transfer of the catalysts. The macroscopic size and shape is relevant for properties such as pressure drop (fixed-bed reactor), mechanical strength, and attrition resistance.

In catalyst manufacturing a final catalyst is usually obtained in multiple steps. Building blocks of the final catalyst may be obtained from sol-gel type processes with support materials such as alumina and silica as prime examples. Also, zeolites and carbon are relevant catalyst building

Table 1.3 Generations of solid catalysts according to manufacturing techniques.

Period	Material type	Key production step	Example – material and process
~1890	Natural	Shaping	Bauxite; Claus process
~1930	Natural	Shaping	Clays; catalytic cracking
~1940	Synthetic	Impregnation	Pt/Al ₂ O ₃ ; reforming
~1970	Synthetic	Precipitation	Cu/ZnO/Al ₂ O ₃ ; methanol synthesis
~1980	Synthetic	Hydrothermal	ZSM-5; methanol-to-gasoline
>2000	Nanostructured	Templating, CVD	MCM-41, SBA-15, CNF, CNT

See main text for an explanation of abbreviations.

blocks. The synthesis of these “building blocks” mostly leads to primary particles in the nanometer or micrometer range that have to be shaped to macroscopic sizes (Chapter 9). Subsequently, shaped particles can be loaded with active components via methods such as impregnation and drying or ion adsorption.

The development of the manufacture of solid catalyst synthesis is summarized in Table 1.3. The first solid catalysts comprised of supports and active phase available from nature. Bauxite and clays are examples of active phases, while “diatomaceous earth” or “kieselguhr” is a natural source of silica support material. Using sol-gel chemistry synthetic support materials have been developed. Application techniques for the active phase based on impregnation and drying emerged during the twentieth century. Hydrothermal synthesis has been important for synthetic zeolites such as ZSM-5. Using micelle templating nanostructured silica (MCM-41, SBA-15) and other oxides have been produced during the last two decades. Using chemical vapor deposition (CVD) techniques nanostructured carbon materials such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have been produced and explored as catalyst supports [7].

Figure 1.4 displays three generations of support materials, that is, natural silica (kieselguhr), silica gel and ordered mesoporous silica. Moving from natural (Figure 1.4a) to synthetic (Figure 1.4b) materials has greatly improved the control over composition and texture of the support in question. Although diatomaceous earth has been named “nature’s nanotechnology”, one should realize that, next to a low specific surface area and broad pore-size distribution, the variation in properties is a major issue. The latest advancement of synthetic nanostructured supports (Figure 1.4c) has not yet resulted in many new industrial catalysts. For fundamental studies on catalyst preparation, however, these materials are of great value with results that can be translated to more conventional support materials [8].

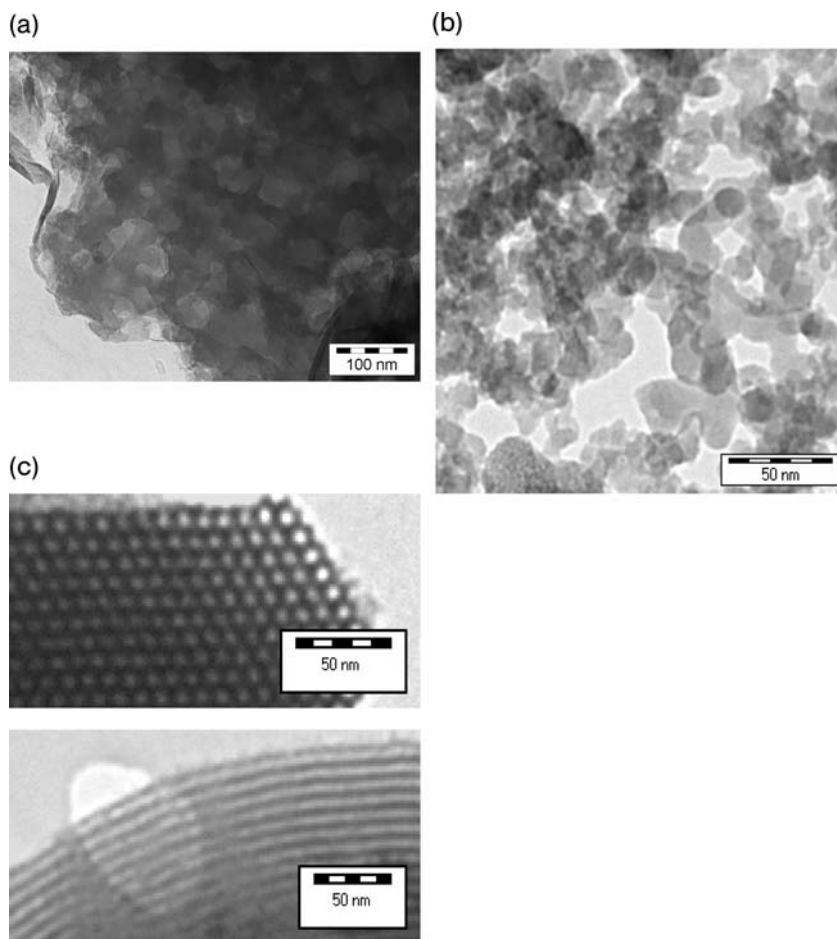


Figure 1.4 Silica materials that have been used catalyst support. (a) Natural silica, kieselguhr ($\sim 20 \text{ m}^2 \text{ g}^{-1}$); (b) silica gel ($\sim 500 \text{ m}^2 \text{ g}^{-1}$); and (c) ordered mesoporous silica, SBA-15 ($\sim 500 \text{ m}^2 \text{ g}^{-1}$).

Here, we illustrate the impact of new supports, on the one hand, and new catalyst synthesis methods, on the other hand, by considering the showcase of the preparation of silica-supported cobalt catalysts for Fischer–Tropsch synthesis. In Figure 1.5 different generations of cobalt catalysts are shown. In Figure 1.5a a kieselguhr-supported cobalt catalyst is shown that has been prepared according to a recipe from the 1940s reported by Anderson [9] that involves precipitation in the presence of the support. The large amount of cobalt separate from the support is apparent as well as clustering of the cobalt particles. Using a synthetic silica gel and impregnation with aqueous cobalt