



# Advanced Catalyst Design II

*A technical investigation commissioned by the members of the Catalytic Advances Program*

## CONTENTS

1. INTRODUCTION.....	1
2. CATALYST DESIGN BASED ON SURFACE SCIENCE AND NANOMATERIALS .....	3
2.1 CATALYST DESIGN BASED ON SURFACE SCIENCE .....	3
2.1.1 Introduction .....	3
2.1.2 Activity vs. Selectivity .....	4
2.1.3 Identification of Relevant Surface Species .....	6
2.1.4 Mechanisms of surface reactions .....	9
2.1.5 Reaction Dynamics at the Atomic Scale .....	10
2.1.6 Use of Model Catalyst Surfaces for Catalyst Design .....	13
2.2 CATALYST DESIGN BASED ON NANOTECHNOLOGY .....	16
2.2.1 Introduction: Synthesis of Nanocatalysts with Tailored Structures .....	16
2.2.2 Control of Metal Clusters at the Atomic Level .....	16
2.2.3 Use of Colloidal Particles, Micelles, and Dendrimers .....	17
2.2.4 Sol-gel and Atomic Layer Deposition (ALD) Synthetic Methods.....	19
2.2.5 Nanolithography, Catalyst Imprinting.....	21
2.2.6 Catalyst Modification: Chiral Catalysis .....	23
2.3 CASE STUDIES OF CATALYST DESIGN BASED ON SURFACE SCIENCE AND NANOTECHNOLOGY INSIGHTS.....	25
2.3.1 Introduction .....	25
2.3.2 Gold nanocatalysts .....	25
2.3.3 Use of Bimetallics to Control Selectivity.....	27
2.3.4 Olefin Epoxidation .....	29
2.3.5 New Advances in Hydrodesulfurization .....	30
2.3.6 Molecular Hydrogen Production .....	32
2.4 CONCLUSIONS AND FUTURE DIRECTIONS .....	34
2.5 REFERENCES .....	37
3. COMPUTATIONAL CATALYST DESIGN .....	45
3.1 INTRODUCTION.....	45
3.2 COMPUTATIONAL TOOLS FOR CATALYST DESIGN.....	45
3.2.1 Quantum Chemical Methods.....	48
3.2.2 Molecular Simulation Methods .....	55

3.2.3	Microkinetic Modeling .....	59
3.3	MODELING THE ACTIVE SITE .....	60
3.4	CASE STUDIES.....	63
3.4.1	Structure-Activity Relationships for Catalyst Design .....	63
3.4.2	Microkinetic Modeling of Ammonia Synthesis .....	65
3.4.3	Stochastic Models of Polymer Growth.....	67
3.4.4	Bimetallic Catalysts for Fuel Cells .....	68
3.5	CONCLUSIONS AND FUTURE DIRECTIONS .....	69
3.6	REFERENCES .....	70
3.7	APPENDIX .....	72
3.7.1	<i>Ab Initio</i> Methods .....	72
3.7.2	Density Functional Theory .....	77
3.7.3	Semi-empirical Methods.....	80
4.	CATALYST DESIGN USING HIGH THROUGHPUT METHODS .....	83
4.1	INTRODUCTION .....	83
4.2	HT LIBRARY DESIGN: TOOLS AND APPROACHES .....	84
4.2.1	Combinatorial Methods: The Split & Pool Approach.....	84
4.2.2	The “Gradient” Approach.....	86
4.2.3	Design of Experiments (DoE) Methodology .....	87
4.2.4	Evolutionary Approach.....	92
4.2.5	Integration of Data Mining Tools in Evolutionary Optimization.....	97
4.2.6	Which is the Best Approach? .....	98
4.3	QSAR APPROACH IN HOMOGENEOUS & HETEROGENEOUS CATALYSIS.....	98
4.3.1	General Concepts.....	99
4.3.2	QSAR Approach in Homogeneous Catalysis .....	99
4.3.3	QSAR approach in heterogeneous Catalysis .....	102
4.4	QUANTITATIVE EVALUATION OF CATALYTIC PROPERTIES .....	105
4.4.1	Motivations for HT Kinetic Screening .....	105
4.4.2	Tools and Strategies for HT Kinetic Modeling .....	106
4.4.3	HT Micro-Kinetic Modeling of Catalysts .....	109
4.5	ELECTRONIC INFRASTRUCTURE FOR HT LABORATORIES AND LARGE ORGANIZATIONS.....	110
4.5.1	Motivation .....	110
4.5.2	Electronic Open Architecture for Tools Integration.....	111
4.5.3	Workflow Based Electronic Architecture for Streamlined Data Processing and Knowledge Management.....	113
4.5.4	Example of Workflow Design and Implementation using Inforsense Technology in a Framework of Virtual Organization for HT Experimentation.....	114
4.6	CONCLUSIONS .....	116
4.7	REFERENCES .....	117
4.8	APPENDIX.....	121
5.	INDEX .....	125

## FIGURES

Figure 2.1	Schematic Energy Diagram For The Cis-Trans Interconversion Of 2-Butenes On Pt(111) Surfaces. ....	5
Figure 2.2	Example Of A Characterization Study Of Catalytic Surfaces In-Situ Under Reaction Conditions. ....	8
Figure 2.3	Proposed Scheme For The Oxidation Of Styrene On O-Covered Au(111) Based On Results From TPD Experiments. ....	9
Figure 2.4	Instrumental Design For Isothermal Measurements Of The Kinetics Of Catalysts On Small Samples. ....	11
Figure 2.5	Example Of The Use Of Model Supported Particles To Emulate The Behavior Of Real Catalysts. ....	14
Figure 2.6	Correlation Between The Surface Concentration And Percentage Of Cationic And Zero-Valent Atoms In Gold-Nanoparticle Catalysts Supported On Magnesium Oxide And Their Catalytic Activity For Carbon Monoxide Oxidation. ....	17
Figure 2.7	Example Of The Preparation Of Designed Catalysts Using Colloidal Chemistry. ....	19
Figure 2.8	Example Of The Use Of Atomic Layer Deposition (ALD) Methods For The Controlled Modification Of Porous Materials. ....	20
Figure 2.9	Schematic Representation Of The Steps Involved In A Mold-To-Mold Cross Imprinting (MTMCI) Process Used To Prepare Supported Platinum Nanoparticles. ....	22
Figure 2.10	Results From A RAIRS Study Of The Adsorption Of Cinchonidine On A Platinum Foil. ....	24
Figure 2.11	An Illustration Of How Scanning Microscopy Can Be Combined With Catalytic Measurements To Establish Structure-Reactivity Correlations And Understand The Physical Properties Responsible For Changes In The Behavior Of Catalysts With Particle Size.....	26
Figure 2.12	Catalytic Turnover Frequencies For The Synthesis Of Vinyl Acetate From Acetic Acid And Ethylene ( $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_4 + 1/2 \text{O}_2 \rightarrow \text{CH}_3\text{COOCHCH}_2 + \text{H}_2\text{O}$ ) On Au(100) And Au(111) Single-Crystals As A Function Of The Amount Of Pd Added To Those Surfaces. ....	28
Figure 2.13	Example Of The Use Of Density Functional Theory (DFT) In The Design Of Selective Catalysts. ....	29
Figure 2.14	STM Images Illustrating The Sites Required For The Adsorption Of Thiophene On $\text{MoS}_2/\text{Au}(111)$ Model Catalysts. ....	31
Figure 2.15	Proposed Reaction Pathways For Production Of $\text{H}_2$ By Reactions Of Oxygenated Hydrocarbons With Water. ....	33
Figure 2.16	Top: Schematic Representation Of Hot Electron Generation By The Exothermic Catalytic Oxidation Of Carbon Monoxide Using A Platinum-Gallium Nitride (Pt/GaN) Nanodiode. Bottom: Experimental Data Measured From The Above System. ....	36
Figure 3.1	Generic Potential Energy Surface For A Chemical Reaction.....	46

Figure 3.2	A Schematic Representation Of How Molecular Modelling Can Be Used To Design A More Active Catalyst Through A Mechanistic Understanding Of The Catalytic Cycle. ....	47
Figure 3.3	Spectrum Of Methods Used To Calculate The Potential Energy Surface. ....	48
Figure 3.4	Schematic Outline Of How The Nuclear Configuration Is Updated In An MD Simulation Of A Diatomic Molecule. ....	56
Figure 3.5	Models For QC Calculations Of A Ni Diimine Catalyst. ....	61
Figure 3.6	Hérisson-Chauvin Mechanism For Olefin Metathesis Adapted For Grubbs Catalysts (Occhipinti Et Al. 2006).....	64
Figure 3.7	Calculated Potential Energy Diagram For The Synthesis Of NH <sub>3</sub> From N <sub>2</sub> And H <sub>2</sub> Over Close-Packed And Stepped Ru Surfaces. . ....	65
Figure 3.8	Relative Contributions To The Rate Of Different Local Environments.. ....	66
Figure 3.9	The Initial Steps Of Polymerization In The Stochastic Model. ....	68
Figure 4.1	(A) Split And Pool Synthesis, (B) Micro-Bead Reactor.....	85
Figure 4.2	Left: Experimental Planning For Catalyst Design. Headers Correspond To The Element Names On The Right; M, O, D And S Stand For Noble Metal, Metal Oxides, Dopants And Supports, Respectively.....	89
Figure 4.3	Left: Blocking Structure Of 19x19 Metal Binary Library. ....	90
Figure 4.4	Example Of Catalyst Encoding As A Chromosome .....	92
Figure 4.5	Genetic Algorithm Workflow For Catalyst Library Design. (“Population” Stands For “Library Of Catalysts” .....	93
Figure 4.6	Effect Of The Population Size On The Optimization Performances From A Simulation Study On The Benchmark Of Wolf. ....	94
Figure 4.7	Screenshot Of A Typical Genetic Algorithm Implemented In Opticat.....	96
Figure 4.8	Concept Of Virtual Screening Embedded In An Optimization Process .....	97
Figure 4.9	Schema Representing The Different Parameter Spaces. Geometrical (Left).....	99
Figure 4.10	Simplified Projection Of The 3D Spaces Representing Catalysts Composition/Structure (Left).....	100
Figure 4.11	“Lego” Design Of Catalyst Of A Bidentate Ligand. Left: The Building Blocks Forming The Template. Right: A Molecular Example.....	101
Figure 4.12	QSAR Approach In Heterogeneous Catalysis .....	103
Figure 4.13	Data Workflow Used To Establish The QSAR Model For Propylene Oxidation Catalysts.....	104
Figure 4.14	Catalyst Classes In The Oxidation Of Propylene. Y Axis .....	105
Figure 4.15	Six Flow Reactor Setup Adapted To Fast Kinetic Studies .....	107
Figure 4.16	Schema Of The SWITCH 16 Setup .....	108
Figure 4.17	Examples Of Fast Transient Investigations Using 16-Parallel Reactors. ....	109
Figure 4.18	Reaction Modeling Suite.....	110
Figure 4.19	Data Workflow Design Which Shows Data Sources, Aggregation, Processing And Visualization .....	115
Figure 4.20	Left: Dynamic Visualization Of Post-Process Data. Right: Parity Diagrams Show The Adequacy Of The Agreement Between The Experimental And Modelled Data (Right) .....	116

## TABLES

Table 4.1	Binary Composition At The First Screening. ....	86
Table 4.2	Definition Of The Parameter Search Space For The First Screening Round For Hydrogenation Catalysts (Veum, 2006).....	88
Table 4.3	Definition Of The Parameter Search Space For The Second Screening Round For Hydrogenation Catalysts (Veum, 2006).....	88