Chemical Kinetics and Catalysis

R. A. van Santen and J. W. Niemantsverdriet

Schuit Institute of Catalysis Eindhoven University of Technology Eindhoven, The Netherlands

Plenum Press • New York and London

CONTENTS

CHAPTER 1. THE SCIENCE OF CATALYSIS

1.1.	Introduction	•	•	•	•	•	•	•	•	•	•	•	•	1
1.2.	The Early Days of Catalysis	•	•			•	•			•		•		3
1.3.	Kinetics and Chemical Thermodynamics		•	•						•		•	•	6
1.4.	The Ammonia Synthesis		•	•				•	•					9
1.5.	Catalysis and the Growth of the Chemical Industry	•	•		•	•		•	•	•	•	•		10
1.6.	The Scientific Disciplines of Catalysis	•	•	•		•	•	•						14
1.7.	The Scope of This Book	•	•	•	•	•	•	•		•	•			18

CHAPTER 2. THE RATE EQUATION

2.1.	The Reaction Equation			•	•			•	•		•		21
2.2.	The Second Law of Thermodynamics				•						•	•	26
2.3.	Coupled Reactions and the Steady-State Assumption			•	•			•			•	•	28
2.4.	Chain Reactions							•				•	35
2.5.	Parallel and Consecutive Reactions									•			38
2.6.	Principle of Catalysis												43
2.7.	Steady States Far from Equilibrium; Autocatalysis .	•				•		•			•	•	58
	2.7.1. Autocatalysis and Oscillating Reactions		•				•				•	•	59
	2.7.2. Oscillating Surface Reactions				•							•	66

CHAPTER 3. INTRODUCTION TO CATALYTIC REACTIONS

3.1.	Catalysis by Metals	. 74
	3.1.1. Chemisorption on Metal Surfaces	. 74
	3.1.2. Hydrogenation and Related Reactions	. 79
	3.1.2.1. Ammonia Synthesis	. 79

CONTENTS

	3.1.2.2. Synthesis Gas Conversion	1
	3.1.2.3. Hydrocarbon Activation	3
	3.1.2.4. Oxidation	7
3.2.	Catalysis by Oxides	9
	3.2.1. Chemisorption on Oxides	9
	3.2.2. Catalytic Reactions on Oxides	3
	3.2.3. Solid Acid Catalysis	7
3.3.	Catalysis by Sulfides	2

CHAPTER 4. COLLISION AND REACTION-RATE THEORY

4.1.	Microscopic Theory and Thermodynamics
4.2.	Partition Functions
	4.2.1. Partition Function of an Ideal Monoatomic Gas 112
	4.2.2. Classical Partition Function of a Diatomic Molecule 114
	4.2.3. The Quantum-Mechanical Partition Function of the Diatomic
	Molecule
4.3.	Microscopic Expressions for the Rate Constant
	4.3.1. The Rate Expression
	4.3.2. Collision Theory of Reaction Rates
	4.3.3. Transition-State or Activated Complex Theory
4.4.	Association and Dissociation Reactions: Elementary Reactions on
	Surfaces
	4.4.1. Dissociation and Desorption Reactions
	4.4.2. The Rate of Atomic Adsorption and Desorption
	4.4.3. Rate of Molecular Desorption
	4.4.4. Rate of Dissociation
	4.4.5. Surface Diffusion

CHAPTER 5. MEDIUM EFFECTS ON REACTION RATES

5.1.	Introduction			•	•	 169
	5.1.1. The Chemical Potential of the Activated Complex				•	 170
5.2.	Energy Exchange and Transition-State Theory			•	•	 172
5.3.	Kramers' Reaction-Rate Theory			•	•	 179
5.4.	Rate of Vibrational Energy Transfer between Gas Molecules			•	•	 187
5.5.	The Surface Thermal Accommodation Coefficient	•		•	•	 194
5.6.	Marcus Theory of Proton and Electron Transfer in Liquids .	•	•	•	•	 197
5.7.	Surface Overlayers and Inhomogeneity				•	 201
	5.7.1. Long-Range Coadsorbate Effects					 201
	5.7.2. Short-Range Coadsorbate Interaction		•	•	•	 206

CONTENTS

CHAPTER 6. MICROSCOPIC THEORY OF HETEROGENEOUS CATALYSIS

6.1.	Prediction of the Overall Rate of a Catalytic Reaction	213
6.2.	The Elementary Rate of Adsorption	217
6.3.	Dissociative Adsorption	223
	6.3.1. Introduction	223
	6.3.2. Molecular Orbital Picture of Chemisorption	224
	6.3.3. Chemistry of Surface Dissociation	228
	6.3.4. Chemical Precursor-Assisted Dissociation	231
	6.3.5. Dynamics of Dissociation; Quantum-Mechanical Tunneling	233
	6.3.5.1. The Dissociation of Hydrogen by Copper	233
	6.3.5.2. The Tunneling Correction to the Rate Constant in the	
	Transition-State Theory	235
6.4.	Transition States of Surface Reactions	238
	6.4.1. The Transition State for Methane Dissociation on a Metal	238
	6.4.2. The Transition State for Methane Activation by Brønsted-Acid	
	Protons	243
6.5.	Kinetics of Dissociative Adsorption	247
6.6.	Catalytic Reactions	253
	6.6.1. The Hougen–Watson Approach	253
	6.6.2. Competitive Adsorption in Hydrocarbon Catalysis	256
	6.6.3. Volcano Curve for the Synthesis of Ammonia	260
	6.6.4. Selectivity Control by Competitive Adsorption	261
	6.6.5. Selectivity in the Fischer–Tropsch Synthesis	264
REI	FERENCES	269
Kela	ated Reading: General Texts on Kinetics and Catalysis	271
IND	DEX	273

~