

Contents

Part I Fundamentals and Techniques

1 Fundamentals in Adsorption at the Solid–Gas Interface. Concepts and Thermodynamics	3
Vera Bolis	
1.1 Introduction	3
1.2 The Solid Surface	4
1.2.1 Porous Materials	5
1.3 Adsorption Processes	7
1.3.1 Adsorption Isotherms	8
1.4 Adsorption Microcalorimetry	14
1.4.1 Materials	15
1.4.2 Equilibrium Data	18
1.5 Thermodynamics of Adsorption	29
1.5.1 Heat of Adsorption from Direct Calorimetric Methods	30
1.5.2 Heat of Adsorption from Indirect Non-Calorimetric Methods	32
1.5.3 Entropy of Adsorption	33
1.6 Adsorption of a Single Component: Physisorption Versus Chemisorption	38
1.7 Conclusions	44
References	45
2 Thermal Analysis and Calorimetry Techniques for Catalytic Investigations	51
Pierre Le Parlouër	
2.1 Introduction	51
2.2 Thermal Analysis and Calorimetry: Techniques and Applications	52
2.3 The Differential Thermal Analysis Technique	53
2.3.1 Principle	53
2.3.2 Detectors	56

2.3.3	Operation	57
2.3.4	Applications	57
2.4	The Differential Scanning Calorimetry Technique	58
2.4.1	Principle	58
2.4.2	Detectors	61
2.4.3	Operation	64
2.4.4	Applications	67
2.5	The Calorimetric Techniques	70
2.5.1	Calorimetric Principles	70
2.5.2	Isothermal Calorimetry	72
2.5.3	Isothermal Titration Calorimetry	80
2.6	The Thermogravimetric Technique	81
2.6.1	Principle	81
2.6.2	Detectors	83
2.6.3	Operation	85
2.6.4	Applications	87
2.7	The Simultaneous Techniques	89
2.8	Evolved Gas Analysis	92
2.8.1	TG-MS Coupling	93
2.8.2	TG-FTIR Coupling	97
2.9	Conclusion	98
	References	99
3	Couplings	103
	Dušan Stošić and Aline Auroux	
3.1	Introduction	103
3.2	Coupled Calorimetry–Volumetry	104
3.3	Coupled Calorimetry–Gravimetry	112
3.4	Temperature Programmed Desorption Technique	113
3.5	Temperature Programmed Reduction	115
3.6	Calorimetry–Gas Chromatography/Mass Spectrometry	116
3.7	Calorimetry–Syringe Pump–UV–Vis Fluorescence Spectrometry	117
3.8	Limitations of Technique	121
3.9	Influence of the Adsorption Temperature on the Acid/Base Determination	122
3.10	Probe Molecules	123
3.10.1	Probing Surface Acidic Properties	123
3.10.2	Probing Surface Basic Properties	125
3.10.3	Probing Surface Redox Properties	126
	References	126

4	Temperature-Programmed Desorption (TPD) Methods	131
	Vesna Rakić and Ljiljana Damjanović	
4.1	Introduction	132
4.2	Adsorption–Desorption; Fundamental Principles	134
4.2.1	Thermodynamic View	135
4.2.2	Kinetics of Adsorption and Desorption	136
4.3	Experimental Setups	138
4.4	The Design of Temperature-Programmed Experiment; Obtained Data.	140
4.4.1	The Design of TPR/TPO Experiments; Obtained Data. . .	144
4.5	The Interpretation of Results Obtained from Temperature-Programmed Desorption Experiments	145
4.5.1	The Application of Temperature-Programmed Desorption in Active Sites Characterisation	146
4.5.2	The Application of TPD in the Determination of Kinetic and Thermodynamic Parameters of Desorption Processes.	154
4.6	The Examples of TPD Application; the Comparison with Data Obtained by Adsorption Calorimetry.	162
4.6.1	Zeolites	163
4.6.2	Metal Oxides	167
4.6.3	Metals	169
4.7	Conclusion	171
	References	171
5	Temperature Programmed Reduction/Oxidation (TPR/TPO) Methods	175
	Antonella Gervasini	
5.1	Redox Properties of Metal Oxides and Catalytic Implications. . .	175
5.2	Temperature-Programmed Reduction/Oxidation Technique. . . .	180
5.2.1	General Operative Procedure	181
5.2.2	Analytical Parameters	183
5.2.3	Selection of Operating Parameters.	185
5.3	Kinetics and Reduction Mechanisms	186
5.3.1	Nucleation Model	188
5.3.2	Contracting Sphere Model	188
5.4	Examples	190
	References	195
6	Calorimetry at the Solid–Liquid Interface.	197
	Jerzy Jozef Zajac	
6.1	Introduction	197
6.2	Thermodynamic Treatment of the Solid–Liquid Interface and the Related Interfacial Phenomena.	199

6.2.1	Surface Excess Functions and Surface Phase Model	199
6.2.2	Adhesion and Cohesion	203
6.2.3	Wetting in Solid–Liquid Systems	208
6.2.4	Hydrophobic and Hydrophilic Substances	210
6.3	Calorimetry Applied to Evaluate Surface Properties of Solids. . .	210
6.3.1	Enthalpy Changes in the Thermodynamic Cycle of Immersion-Adsorption–Wetting	212
6.3.2	Immersional and Wetting Calorimetry Experiments. . . .	214
6.3.3	Hydrophilic-Hydrophobic Series and Harkins-Jura Method	219
6.4	Enthalpy Changes Accompanying Competitive Adsorption from Dilute Solution	224
6.4.1	Thermal Properties of Dilute Solutions	225
6.4.2	Macroscopic Description of Competitive Adsorption. . .	229
6.4.3	Competitive Adsorption Measurements	231
6.4.4	Immersion in Dilute Solutions	234
6.4.5	Model of Flow Calorimetry Experiment.	236
6.4.6	Model of Batch Calorimetry Experiment	240
6.5	Calorimetry Applied to Study Competitive Adsorption from Dilute Solution	247
6.5.1	Flow Calorimetry System.	247
6.5.2	Measurements of Integral Enthalpy of Displacement. . .	250
6.5.3	Titration Calorimetry System	254
6.5.4	Scanning of Surfactant Aggregation by Titration Calorimetry	258
6.6	Concluding Remarks	263
	References	264

Part II Applications and Case Studies

7	Study of Selective Adsorption of Gases by Calorimetry	273
	Jean-Pierre Bellat	
7.1	Introduction	273
7.2	Definition of Selective Adsorption.	274
7.2.1	Adsorption of Single Component	274
7.2.2	Adsorption of Gas Mixtures	278
7.3	Adsorption Enthalpies and Entropies	282
7.3.1	Adsorption Enthalpy	283
7.3.2	Adsorption Entropy and Molar Adsorbate Entropy	283
7.4	Calculation of Adsorption Enthalpy and Entropy from Single Adsorption Isotherms	284
7.4.1	Van't Hoff Method	285
7.4.2	Isosteric Method So-called Clausius-Clapeyron Method	286

7.5	Determination of Coadsorption Enthalpy and Entropy by Calorimetry	288
7.5.1	Experimental Calorimetric Technique	288
7.5.2	Measurement of Adsorbed Amounts	289
7.5.3	Measurement of Differential Adsorption Enthalpy.	292
7.5.4	Adsorption Gibbs Energy	297
7.5.5	Differential Adsorption Entropy and Molar Entropy of Adsorbate.	302
7.5.6	Partial Adsorption Enthalpy and Entropy	303
7.6	Case Studies	305
7.6.1	Separation of Xylenes Isomers by Selective Adsorption on FAU Type Zeolite	305
7.6.2	Desulphurization of Natural Gas by Selective Adsorption on FAU Type Zeolite	311
7.7	Conclusions	317
	References	318
8	Characterization of Acid–Base Sites in Oxides	319
	Antonella Gervasini	
8.1	Introduction	319
8.2	The Surface Acido–Basicity of Metal Oxides	320
8.3	Acid, Basic, and Amphoteric Oxides	323
8.4	Heterogeneous Character of Oxides	325
8.5	Single Oxides, Doped and Modified Oxides, Supported Oxides, Mixed Oxides, and Complex Oxides	330
8.6	Acidity Prediction from Composition	343
8.7	Intrinsic and Effective Acidity of Oxide Surfaces	346
	References	349
9	Characterization of Acid–Base Sites in Zeolites	353
	Dušan Stošić and Aline Auroux	
9.1	Introduction	353
9.2	Factors Influencing the Acid Properties of Zeolites	356
9.2.1	Influence of the Zeolite Topology	357
9.2.2	Influence of the Si/Al Ratio	359
9.2.3	Influence of the Pre-treatment Parameters	365
9.2.4	The Effect of Proton (Cation) Exchange Level	368
9.2.5	The Influence of the Framework T Atom	370
9.3	Correlation Between Adsorption Heat and Catalytic Activity	376
	References	378

10 Adsorption/Desorption of Simple Pollutants	385
Vesna Rakić	
10.1 Introduction	385
10.1.1 Possible Abatement Procedures.	387
10.2 The Application of Calorimetry in Environment Protection	389
10.2.1 Calorimeters Can be Applied for Direct Investigation of Some Event that Includes Specific Pollutant(s).	390
10.2.2 Calorimeters Can be Applied for the Characterization of Solid Materials	398
10.3 The Application of Temperature-Programmed Techniques in Environment Protection	400
10.4 The Application of Thermo-analytical Methods in Environment Protection	402
10.5 Conclusion	405
References	405
11 Hydrogen and Calorimetry: Case Studies	409
Simona Bennici and Aline Auroux	
11.1 Introduction	409
11.2 First Case Study: Irreversible H ₂ Storage (Borohydrides).	411
11.2.1 Hydrolysis of NaBH ₄ Stabilized Solutions	411
11.2.2 Hydrolysis of NaBH ₄ and KBH ₄ Powders	416
11.3 Second Case Study: Reversible H ₂ Storage (Mg-Based Materials)	422
11.4 Conclusions	426
References	426
12 Adsorption Microcalorimetry as a Tool to Study the CO–Pt Interaction for PEMFC Applications: A Case Study	429
Georgeta Postole and Aline Auroux	
12.1 Evolution and Types of Fuel Cell	429
12.2 Proton Exchange Membrane Fuel Cells	433
12.3 CO Adsorption Microcalorimetry on Pt-Based Materials: Literature Survey.	437
12.4 The CO Poisoning Effects on Pt/C Studied by Adsorption Microcalorimetry: A Case Study	441
12.5 Summary	450
References	450
13 Biodiesel: Characterization by DSC and P-DSC	455
Rodica Chiriac, François Toche and Christian Brylinski	
13.1 Introduction	455
13.2 Study of the Cold Flow Behavior of Biodiesel by DSC and Thermomicroscopy	458

13.2.1	Introduction	458
13.2.2	Experimental Procedures	460
13.2.3	DSC and Thermomicroscopy for the Study of Biodiesel and Biodiesel Blends.	461
13.2.4	Conclusions	468
13.3	Oxidative Stability of Biodiesel by P-DSC	469
13.3.1	Introduction	469
13.3.2	Experimental Procedure	472
13.3.3	Results and Discussions	473
13.3.4	Conclusion	476
13.4	Overall Conclusion	476
	References	477
14	CO₂ Capture in Industrial Effluents. Calorimetric Studies	481
	Jean-Yves Coxam and Karine Ballerat-Busserolles	
14.1	Introduction	481
14.2	Presentation of Techniques for CO ₂ Separation from Gaseous Effluents	482
14.3	Industrial Processes Proposed for CO ₂ Capture in Post Combustion Effluents	484
14.4	Thermodynamic Approach of CO ₂ Dissolution in Aqueous Solutions of Amine	485
14.4.1	Mechanism of CO ₂ Dissolution	485
14.4.2	Selection of Amines for CO ₂ Capture Processes	486
14.4.3	Calorimetric Experimental Data Required	487
14.5	Calorimetric Studies of CO ₂ Dissolution in Amine Solutions	490
14.5.1	Calorimetric Techniques for Measuring Heat of Mixing.	490
14.5.2	Calorimetric Investigations.	494
14.6	Conclusion	499
	References	500
15	Adsorption Microcalorimetry, IR Spectroscopy and Molecular Modelling in Surface Studies	505
	Vera Bolis	
15.1	Introduction	505
15.2	CO Adsorbed on Coordinatively Unsaturated Metal Cations	506
15.3	NH ₃ Adsorbed on All-Silica MFI Zeolites (Silicalite)	512
15.4	H ₂ O Vapor Adsorbed on Crystalline and on Amorphous Alumino-Silicates	514
15.5	Conclusions	516
	References	517

16 Characterisation of Catalysts and Adsorbents by Inverse Gas Chromatography	521
Eva Díaz and Salvador Ordóñez	
16.1 Introduction	521
16.2 Experimental.	522
16.3 Adsorption Isotherms	526
16.4 Thermodynamic Parameters	529
16.4.1 Retention Volume	529
16.4.2 Free Energy of Adsorption	531
16.4.3 Enthalpy and Entropy of Adsorption	531
16.4.4 Work of Adhesion: Dispersive and Specific Contribution	533
16.4.5 Surface Heterogeneity	537
16.5 Applications and Comparison to Other Techniques	538
References	540
17 Liquid–Solid Adsorption Properties: Measurement of the <i>Effective Surface Acidity</i> of Solid Catalysts.	543
Paolo Carniti and Antonella Gervasini	
17.1 Introduction	543
17.2 Pulse Liquid Chromatographic Method	545
17.3 Liquid Recirculation Chromatographic Method	547
17.4 Concluding Remarks	550
References	551
Index	553

Calorimetry and Thermal Methods in Catalysis

Auroux, A. (Ed.)

2013, XVI, 561 p. 312 illus., 85 illus. in color., Hardcover

ISBN: 978-3-642-11953-8