Table of Contents

Preface v
About the authors and contributors vii

1. Introduction 1

1.1 Fine particle technology 1
1.2 Particle size 3
1.3 Surfacearea 5
1.4 Pore size and volume 7
1.5 Density. 9
1.6 Chemisorption 11
1.7 Electrophoretic mobility 14
1.8 Contact angle 16

2. Particle Size by Sedimentation 17

2.1 Introduction 17
2.2 Theory 18
2.3 General description 20
2.4 Sample preparation 23
2.4.1 Selecting the proper liquid medium 25
2.4.2 Dispersion 26
2.4.3 Surfactants and other dispersing agents 27
2.4.4 Magnetic samples 29
2.5 Making a test 30
2.6 Batch sampling 30
2.7 Analysis reports 31
2.7.1 Summaries 31
2.7.2 Tabular data 32
2.7.3 Cumulative data 32
2.7.4 Determination of mass, area, and number 33
2.7.5 Histograms 34
2.7.6 Differential plots 34
2.7.7 Size distribution functions 34
2.7.7.1 Normal distribution 36

2.7.7.2 Log normal distribution 37
2.7.7.3 Rosin-Rammler plot 38
2.7.8 Comparative information 39
2.7.9 Statistical process control charts 39
2.8 Recognizing anomalous results 40
2.8.1 Sample-related effects 41
2.8.2 Flocculation and agglomeration 42
2.8.3 Inappropriate liquid medium 43
2.8.4 Maintenance-related effects 45
2.8.5 Limitations of the technique 45
2.9 X-ray safety 48
Symbols used in this chapter 49
References 51

3. Surface Area and Pore Structure by Gas Adsorption 53

3.1 Introduction 53
3.2 The adsorption isotherm 55
3.3 Adsorption theory and methods of extracting information from the adsorption isotherm 59
3.3.1 Langmuir theory 59
3.3.2 BET theory 60
3.3.3 Standard isotherms, t-, and as-plots 63
3.3.4 Thickness equations 67
3.3.5 Methods of characterization for microporous materials 70
3.3.5.1 MP Procedure 71
3.3.5.2 Dubinin-Radushkevich method 71
3.3.5.3 Dubinin-Astakhov analysis 73
3.3.5.4 Horvath-Kawazoe equation 73
3.3.5.4.1 The cylindrical pore model extension of Saito and Foley 75
3.3.5.4.2 The spherical pore model extension of Cheng and Yang 76
3.3.5.4.3 The method of Cheng and Yang in regard to nonlinearity 77
3.3.6 Methods of characterizing mesoporous and macroporous materials 78
3.3.6.1 Kelvin equation 79
3.3.6.2 BJH method 80

3.3.7 Density functional theory 81
3.3.8 Fitting model isotherms to experimental data by the method of deconvolution 87
3.3.9 Surface energy distribution 89
3.3.10 Rate of adsorption 90
3.4 Measurement of the isotherm 91
3.4.1 Application of gas laws 91
3.4.2 Standard volume 92
3.4.3 Nonideality 92
3.5 Instrumental methods and theory of instrument design 93
3.5.1 Static volumetric method 94
3.5.1.1 Determining the manifold volume 95
3.5.1.2 Determining the quantity of gas in the free space of the sample holder 98
3.5.1.2.1 Warm free space 100
3.5.1.2.2 Determining the quantity of gas at cryogenic temperature 101
3.5.1.2.3 Cold free space 103
3.5.1.3 Determining the quantity of gas adsorbed 103
3.5.1.4 Control of cryogen level during tests 105
3.5.1.5 Thermal transpiration 107
3.5.1.6 Single sample volumetric analyzer. 108
3.5.1.6.1 The analysis gas manifold 109
3.5.1.6.2 Software control of the dosing and pressure equilibration routines 110
3.5.1.6.2.1 Dosing by pressure table 111
3.5.1.6.2.2 Incremental dosing 111
3.5.1.6.2.3 Fixed-quantity dosing 112
3.5.1.6.2.4 Dose-sensitive data collection 112
3.5.1.6.2.5 Equilibrium detection 112
3.5.1.7 Making a test 115
3.5.1.7.1 Saturation pressure measurement 115
3.5.1.7.2 Free-space determination 116
3.5.1.7.3 Determination of gas-adsorbed quantity 116
3.5.2 The multiple-port volumetric analyzer 117
3.5.3 The Gemini design 118
3.5.4 The flowing-gas (dynamic) analyzer 121
3.5.4.1 Design features 122
3.5.4.2 Applying Dalton's law of partial pressures 122
3.5.4.3 Calibration 124

3.5.4.4 Making a test 124
3.6 Recognition and avoidance of problems 126
3.6.1 Leaks 126
3.6.2 Instrument calibration 127
3.6.3 Connecting an adsorptive gas supply to the instrument . . 128
3.6.4 Sample preparation 129
3.6.5 Helium entrapment. 131
3.6.6 Use of SealFrits and PrepSeals 132
3.6.7 Selecting the appropriate adsorptive 133
3.6.7.1 Krypton and argon vs. nitrogen for low surface area determinations 133
3.6.7.2 Nitrogen vs. argon for micropore analyses 134
3.6.8 Cryogen and adsorptive pairing 135
3.6.9 Sample temperature 135
3.6.10 Sample quantity 135
3.6.11 Free-space values 136
3.6.12 Thermal transpiration correction 137
3.6.13 Equilibrium time 137
3.6.14 Measured vs. entered saturation pressure 139
3.7 Evaluation of results 139
3.7.1 Inspection of the isotherm plot 140
3.7.2 Evaluating the isotherm tabular dam set. 140
3.7.3 Reduced data 141
3.7.3.1 Physical parameters 141
3.7.3.2 Guidelines and evaluation of data reduction methods 142
3.7.3.3 BET C-value. 143
3.7.3.4 Data analyses by the BJH method 143
3.8 **A** systematic approach to sample analyses by physical adsorption 144
3.8.1 Sample preparation 144
3.8.2 Analysis temperature 144
3.8.3 Quantity of sample 145
3.8.4 Surface area determination 145
3.8.5 Porosity 146
Symbols used in this chapter 147
References. 152

4. Pore Structure by Mercury Intrusion Porosimetry (MIP) 155
4.1 Introduction 155

4.2 Theory 156
4.3 Other derivable information 159
4.4 Instrument description 161
4.5 Operation 164
4.5.1 Scanning 164
4.5.2 Set-time equilibration 165
4.5.3 Set-rate equilibration 166
4.5.4 Data collection modes 166
4.6 Compensation factors 167
4.7 Results 168
4.7.1 Comparison of mercury porosimetry and gas adsorption results 172
4.7.2 Particle mass percent distribution by size 174
4.7.3 Pore shape distribution by neck and inner cavity size . . . 175
4.8 Getting good results 176
4.8.1 Mercury purity 177
4.8.2 Confirming instrument calibration and general operation . 177
4.8.3 Compatibility of mercury and the sample material 178
4.8.4 Matching penetrometer to sample 178
4.8.5 Sample preparation 179
4.8.6 Thermal effects. 179
4.8.7 Samples subject to structural failure 180
4.8.8 Optimizing the equilibration rate 180
4.8.9 Choosing the data collection mode 180
4.8.10 Optimizing crossover pressure 181
4.8.11 Spacing of data points. 181
4.9 Assessment of experimental data 181
4.9.1 Flat regions and spikes on the intrusion or extrusion curve 182
4.9.2 Abrupt vertical data excursion 182
4.9.3 Negative intrusion and positive extrusion data 183
4.10 Interpretation of analytical data 183
4.10.1 Cumulative intrusion volume vs. diameter 183
4.10.2 Incremental intrusion volume vs. diameter 184
4.10.3 Differential intrusion volume vs. diameter 184
4.10.4 Log differential intrusion volume vs. diameter 185
4.10.5 Incremental pore area vs. diameter 185
4.10.6 Log differential pore area vs. diameter 186
4.10.7 Other calculated data reports 186
4.11 Proper handling of mercury 187
4.12 A systematic approach to sample analyses 188

Symbols used in this chapter 190
References 191

5. Density 193
5.1 Introduction 193
5.2 Densities defined 193
5.3 Absolute density 195
5.3.1 Automatic pycnometers 195
5.3.1.1 Theory 197
5.3.1.2 Applications 199
5.3.2 Manual pycnometer 200
5.3.3 Error avoidance 201
5.3.3.1 Thermal effects 201
5.3.3.2 Sample outgassing during analysis and the effects of vapor pressure 202
5.3.3.3 Highly adsorptive samples 202
5.3.3.4 Leaks 203
5.3.3.5 Permeable samples 203
5.3.3.6 Compressible samples 203
5.3.3.7 Thermally sensitive samples 203
5.3.3.8 High surface area samples 204
5.3.3.9 Improper sample quantity 204
5.3.3.10 Improper calibration 205
5.4 Envelope density 205
5.4.1 Theory 205
5.4.2 General description 206
5.4.3 Calibration 208
5.4.4 Applications 209
5.4.5 Error avoidance 211
5.4.5.1 Sample cylinder selection 211
5.4.5.2 Sample quantity optimization 212
5.4.5.3 Calibration 212
5.4.5.4 Pretest sample preparation 212
5.5 Bulk density 213
5.5.1 Wall effect 214
5.5.2 Repetitive cycles 215
5.5.3 Moisture Content 215
5.5.4 Assessing Compaction Behavior 216
Symbols used in this chapter 217
References 218

6. Chemical Adsorption 219

6.1 Introduction 219
6.2 Physical and chemical adsorption differentiated 219
6.3 Theory 221
6.3.1 Chemisorption and its energies 221
6.3.2 Classical theories of chemical adsorption isotherms 222
6.3.2.1 Langmuir theory 222
6.3.2.2 Freundlich and Temkin isotherms 224
6.4 Analysis and data reduction 225
6.4.1 Static volumetric 225
6.4.1.1 Isolating the chemisorption isotherm 226
6.4.1.2 Chemisorption monolayer volume 226
6.4.1.3 Number of accessible active sites 227
6.4.1.4 Metal dispersion 228
6.4.1.5 Active metal area 229
6.4.1.6 Active particle size 229
6.4.1.7 Isosteric heat of adsorption 230
6.4.2 Dynamic technique: pulse chemisorption 231
6.4.3 Temperature-programmed reactions 232
6.4.3.1 Temperature-programmed reduction 232
6.4.3.2 Temperature-programmed desorption 235
6.4.3.3 Temperature-programmed oxidation 236
6.5 Instrumentation 236
6.5.1 Dynamic (flowing gas) instruments 236
6.5.2 Instrumentation for the study of temperature-programmed reactions 239
6.5.2.1 Relation of function to valves and flow paths 239
6.5.2.2 Temperature controlled internal modules 242
6.5.2.3 Temperature monitoring 243
6.5.2.4 Thermal conductivity detector 243
6.5.2.5 Response times and synchronization 245
6.5.2.6 Subambient analysis 246
6.5.2.7 Monitoring and controlling gas flow 246
6.5.2.8 Mixed gases 247
6.5.2.9 Vapor generation 247
6.5.3 Static volumetric chemisorption analyzer 247
6.5.3.1 Gas delivery system 248
6.5.3.2 Materials of construction 249
6.5.3.3 Sample holder assembly 249

6.5.3.4 Sample temperature 249
6.5.3.5 Sample degassing, pretreatment, and analysis 250
6.6 Analytical techniques and data reduction methods 250
6.6.1 Measurement of surface acidity by ammonia titration . . . 250
6.6.2 TPD applied to the distribution of acid site strength 251
6.6.3 Determination of isosteric heat of adsorption 253
6.6.4 Active Surface area and percent dispersion of metal oxides by the dynamic technique 257
6.6.5 Sample preparation 257
6.6.6 Analysis. 258
6.6.7 Data reduction 258
6.6.7.1 Quantifying reaction gas volumes 258
6.6.7.2 Specific volume chemisorbed 259
6.6.7.3 Total volume of nitrogen produced 259
6.6.7.4 Surface area of copper 259
6.6.7.5 Metal dispersion 260
6.6.8 Temperature-programmed techniques 260
6.6.8.1 TPR of metals on Al_2O_3 260
6.6.8.2 TPD of H_2 from reduced Pt on Al_2O_3 262
6.6.8.3 TPD of ammonia on ZSM-5 zeolite 263
6.6.8.4 TPR of CuO 264
6.6.8.5 TPR of Fe_2O_3 265
6.6.8.6 TPR method for characterizing the interaction between active metal and support 265
6.6.8.7 TPR applied to the formation of alloys 266
6.6.8.8 TPR applied to the study of promoters in bimetallic catalysts 267
Symbols used in this chapter 269
References. 271

7. **Other Measurements** 273

7.1 Introduction 273
7.2 Electrophoretic mobility and zeta potential 273
7.2.1 Background 274
7.2.2 Mass transport theory 274
7.2.3 Description 278
7.2.4 Applications 279
7.3 Contact angle 280
7.3.1 Theory 280
7.3.2 Description 282

7.3.3 Application 282
Symbols used in this chapter 283
References. 284

Index 285