

**Volume 2**

<b>4</b>	<b>Classes of Materials</b>	667
<b>4</b>	<b>Classes of Materials</b>	669
4.1	Clathrates and Inclusion Compounds	669
	<i>H. Gies</i>	
4.1.1	The General Principle of Clathrate Formation	669
4.1.2	Host Structures Built from Organic Molecules	670
4.1.2.1	Hydroquinone Clathrates and Related Compounds	671
4.1.2.1.1	$\beta$ -Hydroquinone Clathrates	671
4.1.2.1.2	$\beta$ -Hydroquinone Clathrate Compounds with Fullerene Guest Molecules	672
4.1.2.1.3	Gossypol	673
4.1.2.1.4	Diamondoid Host Frameworks	674
4.1.2.2	1,3,5-Benzenetricarboxylic Acid	676
4.1.2.2.1	Inclusion Compounds with 1,3,5-Benzenetricarboxylic Acid	676
4.1.2.3	Inclusion Compounds with Alicyclic Diols	678
4.1.2.4	Urea, Thiourea, and Selenourea Inclusion Compounds	680
4.1.2.4.1	Host Framework Structure	680
4.1.2.4.2	Guest Molecules for Urea Inclusion Compounds and its Homologues	681
4.1.2.4.3	The Host–Guest Relation in Urea and Thiourea Inclusion Compounds	681
4.1.3	Inorganic Clathrates and Inclusion Compounds	683
4.1.3.1	Werner Clathrates	683
4.1.3.2	Hydrate Inclusion Compounds	684
4.1.3.2.1	True Clathrate Hydrates	685
4.1.3.2.2	Ionic Clathrates	686
4.1.3.2.3	Semiclathrates	687
4.1.3.3	Cyanometallates	688
4.1.3.3.1	Host Frameworks with Square Planar $[Ni(CN)_4]^{2-}$	689
4.1.3.3.2	Host Frameworks with Tetrahedral $[Cd(CN)_4]^{2-}$	690
4.1.3.4	Silica-based Inclusion Compounds	691
4.1.3.4.1	Silica Host Frameworks	692
4.1.3.4.2	Guest Molecules for the Synthesis of Silica Inclusion Compounds	693
4.1.3.5	Relation between Different Inclusion Compounds with Tetrahedral Host Frameworks	695
4.1.4	Final Remarks	696
	References	696
4.2	Crystalline Microporous Solids	699
4.2.1	Introduction and Structure	699
	<i>W. Depmeier</i>	

4.2.1.1	Introduction	699
4.2.1.2	Structural Basis, Definitions and Databases	699
4.2.1.2.1	Basic Features of Crystalline Microporous Solids	699
4.2.1.2.2	Various Definitions	702
4.2.1.2.3	Databases	715
4.2.1.3	Crystal Chemistry and some Remarks on the Mineral Physics of Poroates	720
4.2.1.3.1	Basic Properties of Tetrahedral Frameworks	720
4.2.1.3.2	Basic Properties of Guests and of Host–Guest Interactions	721
4.2.1.3.3	A Functional Chemical Formula	722
4.2.1.3.4	Silica Frameworks	722
4.2.1.3.5	Zeolite Framework Types and Framework Composition	728
4.2.1.3.6	New Families of Oxidic Nontetrahedral Microporous Solids	732
4.2.1.3.7	The Importance of Weak Forces	732
4.2.1.4	Conclusion	734
	Acknowledgement	734
	References	734
4.2.2	Synthesis of Classical Zeolites	736
	<i>K. Nishi and R. W. Thompson</i>	
4.2.2.1	Introduction	736
4.2.2.2	General Aspects of Synthesis of Zeolites	737
4.2.2.3	Synthesis of Zeolites A, X, and Y	741
4.2.2.4	Kinetics and Mechanisms	743
4.2.2.5	Effect of Seeding on Crystallization	753
4.2.2.6	Effect of Aging of Amorphous Gel on Crystallization	758
4.2.2.7	Effect of Nature of Reactants	762
4.2.2.8	Effect of Alkali Cations	767
4.2.2.9	Addition of Organic Compounds	769
4.2.2.10	Synthesis of Zeolites from Clay Minerals	773
4.2.2.11	Synthesis of Cubic and Hexagonal Analogs of Zeolite Y using Crown-Ethers	774
4.2.2.12	Synthesis using Microwave Heating	777
4.2.2.13	Synthesis of Mordenite	779
4.2.2.14	Synthesis of High-silica Zeolites	786
4.2.2.15	Conclusions	803
	References	804
4.2.3	Synthesis of AlPO <sub>4</sub> s and Other Crystalline Materials	815
	<i>J. Patarin, J. L. Paillaud and H. Kessler</i>	
4.2.3.1	Scope	815
4.2.3.2	History of the Synthesis of 3D Open-Framework Phosphates	815
4.2.3.3	Synthetic Methods	817
4.2.3.3.1	Synthesis Procedures	817
4.2.3.3.2	Chemical Parameters	817
4.2.3.3.3	Physical Parameters	819

4.2.3.4	Aluminophosphates	820
4.2.3.4.1	AlPO <sub>4</sub> - <i>n</i> Materials Reported by Union Carbide Corporation	821
4.2.3.4.2	Other Aluminophosphates Prepared in Aqueous Medium	822
4.2.3.4.3	Aluminophosphates Prepared in a Fluoride Medium	826
4.2.3.4.4	Aluminophosphates Prepared by Solvothermal Synthesis	828
4.2.3.5	Isomorphously Substituted Aluminophosphates	829
4.2.3.5.1	Silicoaluminophosphates (SAPO)	831
4.2.3.5.2	Metalloaluminophosphates (MeAPO) and Aluminometallophosphates (AMePO)	831
4.2.3.5.3	Metallosilicoaluminophosphates (MeAPSO), Element-Aluminophosphates (ElAPO) and Element-Silicoaluminophosphates (ElAPSO)	837
4.2.3.6	Gallophosphates and Isomorphously Substituted Materials	837
4.2.3.6.1	Gallophosphates Prepared with the Conventional Route	837
4.2.3.6.2	Gallophosphates Prepared from a Fluoride-containing Medium	841
4.2.3.6.3	Gallophosphates Prepared in Essentially Nonaqueous Medium	846
4.2.3.6.4	Isomorphously Substituted Gallophosphates	848
4.2.3.6.5	Thermal Stability of the Gallophosphates	849
4.2.3.7	Zincophosphates and Beryllophosphates	852
4.2.3.7.1	Zincophosphates	852
4.2.3.7.2	Thermal Stability of the Zincophosphates	853
4.2.3.7.3	Beryllophosphates	853
4.2.3.8	Proposed Synthesis Mechanisms	856
4.2.3.9	Other 3D Open-Framework Metallophosphates	860
4.2.3.10	3D Open-Framework Metal Phosphonates	862
4.2.3.11	Organized Mesoporous Phosphate-based Materials	865
4.2.3.12	Conclusion and Perspectives	865
	Acknowledgments	865
	References	867
4.2.4	Synthesis of Titanosilicates and Related Materials	876
	<i>M. W. Anderson and J. Rocha</i>	
4.2.4.1	Introduction	876
4.2.4.2	Synthesis	877
4.2.4.3	ETS-10	878
4.2.4.4	ETS-4	881
4.2.4.5	Isomorphous Framework Substitution	882
4.2.4.6	Other Titanosilicates	887
4.2.4.7	Zirconosilicates	890
4.2.4.8	Niobosilicates	891
4.2.4.9	Stannosilicates	891
4.2.4.10	Vanadosilicates	892
4.2.4.11	Other Silicates	893
4.2.4.12	Catalysis	894
4.2.4.13	Optical Properties	896

4.2.4.14	Adsorption Properties	897
4.2.4.15	Cation Exchange	898
4.2.4.16	Conclusions	899
	References	899
4.2.5	Modification of Crystalline Microporous Solids	903
	<i>T. Tatsumi</i>	
4.2.5.1	Ion Exchange and Introduction of Metals into the Pore	904
4.2.5.2	Dealumination and Deboration	913
4.2.5.3	Insertion of Metals into Zeolitic Frameworks	920
4.2.5.4	Control of Pore Size and Inactivation of External Surface	925
4.2.5.5	Organic Modifications	928
4.2.5.6	Conclusions	930
	References	930
4.2.6	Characterization	935
	<i>B. Zibrowius and E. Löffler</i>	
4.2.6.1	Introduction	935
4.2.6.2	Experimental Methods	936
4.2.6.3	Characterization of Selected Features	971
4.2.6.3.1	Structure Elucidation and Identification	971
4.2.6.3.2	Templates and Their Removal	975
4.2.6.3.3	Framework Composition	977
4.2.6.3.4	Acid Sites	983
4.2.6.4	Concluding Remarks	988
	References	990
4.2.7	Characterization of the Pore Width of Zeolites and Related Materials by Means of Molecular Probes	1015
	<i>Y. Traa and J. Weitkamp</i>	
4.2.7.1	Introduction	1015
4.2.7.2	General Aspects	1016
4.2.7.2.1	Dimensions of Probe Molecules and Intracrystalline Cavities	1016
4.2.7.2.2	Molecular Sieving	1018
4.2.7.3	Adsorption of Probe Molecules with Different Size	1020
4.2.7.3.1	Characterization of Various Zeolites in Comparison	1020
4.2.7.3.2	Various Methods for Pore-size Characterization by Adsorption	1025
4.2.7.3.3	Molecular Probes for Zeolites with Different Pore Sizes	1029
4.2.7.4	Catalytic Test Reactions	1033
4.2.7.4.1	Shape-selective Catalysis in Microporous Materials	1033
4.2.7.4.2	Test Reactions for Monofunctional Acidic Molecular Sieves	1037
4.2.7.4.3	Test Reactions for Bifunctional Molecular Sieves	1046
4.2.7.5	Conclusions	1052
	Acknowledgments	1052
	References	1053

4.2.8	Application of Microporous Materials as Ion Exchangers	1058
	<i>W. Schmidt</i>	
4.2.8.1	Ion-Exchange Properties of Zeolites in Aqueous Solutions	1058
4.2.8.2	Aqueous Ion Exchange of Zeolites	1063
4.2.8.2.1	Ion Exchange in Zeolite A	1064
4.2.8.2.2	Ion Exchange in Zeolite X and Zeolite Y	1070
4.2.8.2.3	Ion Exchange in Zeolite P	1076
4.2.8.2.4	Ion Exchange in ZSM-5	1079
4.2.8.3	Nonaqueous Ion Exchange in Zeolites	1084
4.2.8.4	Application of Zeolites as Ion Exchanger	1085
4.2.8.4.1	Detergent Builders	1085
4.2.8.4.2	Waste Water Treatment and Deposition of Heavy Metal Waste	1089
4.2.8.4.3	Preparation of Zeolite Catalysts by Ion Exchange	1090
4.2.8.4.4	Preparation of Adsorbents by Ion Exchange	1091
4.2.8.5	Conclusions	1091
4.2.8.6	Symbols and Abbreviations	1092
	References	1093
4.2.9	Application of Microporous Solids as Catalysts	1097
	<i>J. A. Lercher and A. Jentys</i>	
4.2.9.1	Introduction	1097
4.2.9.2	Direct Influences of the Proximity of Molecule and Zeolites Channel	1100
4.2.9.3	Molecular Sieves as Solid Acids and Bases	1102
4.2.9.3.1	Nature and Origin of Strong Brønsted Acid Sites in Molecular Sieves	1102
4.2.9.3.2	Evidence for Uniformity and Distribution of Acid Sites in Molecular Sieves	1104
4.2.9.4	Acid-catalyzed Reactions	1106
4.2.9.4.1	Activation of Alkanes and Alkenes by Formation of Carbocations	1106
4.2.9.4.2	Reactions Involving Carbon–Carbon Bond Scission in Aliphatic Compounds	1109
4.2.9.4.3	Reactions Involving Formation of Carbon–Carbon Bonds in Aliphatic Compounds	1110
4.2.9.4.4	Reactions Involving Carbon–Carbon Bond Rearrangements	1112
4.2.9.4.5	Positional Isomerization Reactions Involving Hetero-atoms	1115
4.2.9.4.6	Skeletal Isomerization Reactions Involving Hetero-atoms	1115
4.2.9.4.7	Nucleophilic Substitution and Addition Reactions	1117
4.2.9.4.8	Cyclization Reactions	1124
4.2.9.4.9	Electrophilic Substitution on the Aromatic Ring	1125
4.2.9.5	Reactions Catalyzed by Basic Sites	1129
4.2.9.6	Oxidation with Molecular Sieve Catalysts	1134
4.2.9.6.1	Molecular Sieves as Catalysts for Oxidation Reactions	1134
4.2.9.6.2	Ti-containing Molecular Sieves	1134

4.2.9.6.3	Fe-containing Molecular Sieves	1136
4.2.9.6.4	Vanadium-containing Molecular Sieves	1138
4.2.9.6.5	Other Metal-substituted Molecular Sieves	1139
4.2.9.7	Physical Aspects of Molecular Sieve Catalysis for Chemical Synthesis	1140
4.2.9.7.1	General Aspects	1140
4.2.9.7.2	Shape Selectivity	1140
4.2.9.8	Conclusions and Outlook	1145
	References	1145
4.2.10	Applications of Natural Zeolites	1156
	<i>C. Coletta</i>	
4.2.10.1	Introduction and Historical Remarks	1156
4.2.10.1.1	The Early Applications	1156
4.2.10.1.2	The Discovery of Zeolites	1158
4.2.10.1.3	Early Studies in Adsorption and Molecular Sieving	1158
4.2.10.1.4	Early Studies in Ion Exchange	1159
4.2.10.1.5	The Discovery of the Sedimentary Zeolites	1160
4.2.10.2	The Sedimentary Zeolites	1161
4.2.10.2.1	Zeolite Types and Occurrence	1161
4.2.10.2.2	Chemistry and Mineralogy	1162
4.2.10.3	Applications of Sedimentary Zeolites in Adsorption Processes and Catalysis	1166
4.2.10.3.1	Selective Adsorption	1167
4.2.10.3.2	Gas Separation	1167
4.2.10.3.3	Catalysis	1168
4.2.10.4	Applications of Sedimentary Zeolites Based on Ion Exchange	1169
4.2.10.4.1	Wastewater Purification	1169
4.2.10.4.2	Soil Amendment and Soilless Substrate Preparation	1173
4.2.10.5	Applications of Sedimentary Zeolites as Building Materials	1175
4.2.10.5.1	Dimension Stones	1175
4.2.10.5.2	Lightweight Aggregates and Foamed Materials	1177
4.2.10.5.3	Pozzolana-like Materials	1178
4.2.10.6	Applications of Sedimentary Zeolites in Life Sciences	1180
4.2.10.6.1	Animal Science and Nutrition	1180
4.2.10.6.2	Pharmaceutics	1181
4.2.10.6.3	Medical Applications	1182
4.2.10.7	Miscellaneous Uses of Sedimentary Zeolites	1182
4.2.10.8	Summary and Prospects	1182
	References	1183
4.3	Porous Metal-Organic Frameworks	1190
	<i>S. Kaskel</i>	
4.3.1	Introduction	1190
4.3.1.1	Modular Chemistry	1191

4.3.1.2	Network Topologies	1192
4.3.1.3	Rigidity and Dynamics	1193
4.3.1.4	Interpenetration	1194
4.3.1.5	Functionality	1194
4.3.2	Compounds	1194
4.3.2.1	Carboxylates	1195
4.3.2.1.1	Dicarboxylates	1195
4.3.2.1.2	Tricarboxylates	1205
4.3.2.1.3	Tetracarboxylates	1213
4.3.2.1.4	Heterocyclic Carboxylates with N-Donor Functionality	1214
4.3.2.2	N-Donor Ligands	1217
4.3.2.2.1	Four-connected Nets	1217
4.3.2.2.2	T-Shaped Building Blocks and other Three-connected Nets	1222
4.3.2.2.3	Polynuclear Building Blocks	1227
4.3.2.2.4	Reduced Dimensionality and Porosity: Chains	1228
4.3.2.2.5	Porous Zero-Dimensional Frameworks <sup>2</sup>	1229
4.3.2.3	Phosphonates	1229
4.3.2.4	Cyanide Frameworks	1232
4.3.2.4.1	Organometallic Extension	1234
4.3.2.4.2	Cluster Extension	1235
4.3.2.5	Other Ligands	1237
4.3.3	Properties and Applications	1240
4.3.3.1	Sorption Properties and Host–Guest Inclusion	1240
4.3.3.2	Catalysis	1242
4.3.3.3	Sensing	1242
4.3.4	Syntheses	1244
4.3.5	Outlook	1244
	References	1245
4.4	Layered Structures and Pillared Layered Structures	1250
	<i>P. Cool, E. F. Vansant, G. Poncelet, and R. A. Schoonheydt</i>	
4.4.1	Introduction	1250
4.4.2	Layered Crystalline Solids	1253
4.4.2.1	Clay Minerals	1253
4.4.2.2	Layered Double Hydroxides	1255
4.4.2.3	Zirconium Phosphates	1257
4.4.3	Pillaring	1258
4.4.3.1	Definition and Criteria	1258
4.4.3.2	Al-Pillared Smectite Clays	1259
4.4.3.2.1	Aqueous Chemistry of Al <sup>3+</sup> and the Ion-Exchange Reaction	1259
4.4.3.2.2	The Pillaring Process	1261
4.4.3.3	Al-Pillared Vermiculite and Phlogopite Clays	1263
4.4.3.3.1	Pillaring Method	1264
4.4.3.3.2	Interlayer Spacings and Thermal Stability	1264
4.4.3.4	Pillared Layered Double Hydroxides	1265

4.4.3.4.1	Pillaring with POMs	1266
4.4.3.4.2	Organic Preswelling	1268
4.4.3.4.3	Pillaring with Hexacyanometal Complexes	1268
4.4.3.5	Pillared Zirconium Phosphates	1269
4.4.3.6	From Micro- to Mesoporous Pillared Materials	1272
4.4.4	Porosity	1276
4.4.4.1	Isotherms	1277
4.4.4.2	Surface Area	1278
4.4.4.3	Microporosity	1279
4.4.4.3.1	Textural Characteristics of Al-Pillared Clays	1279
4.4.4.4	Mean Micropore Width and Mesopore Size	1282
4.4.4.5	Micropore-Size Distributions	1282
4.4.4.6	Evidence of Porosity by Modern Microscopic Techniques	1287
4.4.5	Adsorption	1291
4.4.5.1	Principles of Adsorption	1291
4.4.5.2	Adsorption in Pillared Clays	1293
4.4.6	Surface Properties	1301
4.4.6.1	Acidity	1301
4.4.6.2	Catalytic Activity	1302
4.4.7	Conclusions	1304
	Acknowledgments	1305
	References	1305