

0053498

CATALYSIS

Science and Technology

Edited by
John R. Anderson and Michel Boudart

Volume 10

With 140 Figures



Springer

Editors

Professor Dr. J.R. Anderson

Chemistry Department
Monash University
Clayton, Victoria 3168
Australia

Professor Dr. M. Boudart

Department of Chemical Engineering
Stanford University
Stanford, CA 94305-5025
USA

ISBN 3-540-60109-0 Springer-Verlag Berlin Heidelberg New York

ISBN 3-540-60440-5 (Set Vols. 1–11)

This work is subject to copyright. All rights are reserved whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its current version, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1996
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Thomson Press (India) Ltd., Madras

SPIN: 10079548 51/3020/SPS 543210 Printed on acid-free paper

Editorial

Our series of books on *Catalysis: Science and Technology* is by now nearly complete. Its purpose has been to collect authoritative and, if possible, definitive chapters on the main areas of contemporary pure and applied catalysis. Its style is not that of an Advances series, nor is it meant to be a collection of up-to-date reviews. If the chapters and the volumes were following each other in a neat, logical order, our series might be considered as trying to emulate the original *Handbuch der Katalyse*, pioneered by Professor G.M. Schwab in the 1940's, or be a new version of *Catalysis*, the series edited by Professor P.H. Emmett in the 1950's. As a matter of expediency, to avoid the delays involved in assembling a complete volume of related chapters, we decided at the outset to publish the chapters as received from our authors.

We submit that, by the time our series is complete, our main objectives will have been met. We are most thankful to all our contributors for their co-operation. The Science and the Technology of Catalysis will prosper as a result of their hard work.

General Preface to Series

In one form or another catalytic science reaches across almost the entire field of reaction chemistry, while catalytic technology is a cornerstone of much of modern chemical industry. The field of catalysis is now so wide and detailed, and its ramifications are so numerous, that the production of a thorough treatment of the entire subject is well beyond the capability of any single author. Nevertheless, the need is obvious for a comprehensive reference work on catalysis which is thoroughly up-to-date, and which covers the subject in depth at both a scientific and at a technological level. In these circumstances, a multi-author approach, despite its well-known drawbacks, seems to be the only one available.

In general terms, the scope of *Catalysis: Science and Technology* is limited to topics which are, to some extent at least, relevant to industrial processes. The whole of heterogeneous catalysis falls within its scope, but only biocatalytic processes which have significance outside of biology are included. Ancillary subjects such as surface science, materials properties, and other fields of catalysis are given adequate treatment, but not to the extent of obscuring the central theme.

Catalysis: Science and Technology thus has a rather different emphasis from normal review publications in the field of catalysis: here we concentrate more on important established material, although at the same time providing a systematic presentation of relevant data. The opportunity is also taken, where possible, to relate specific details of a particular topic in catalysis to established principles in chemistry, physics, and engineering, and to place some of the more important features into a historical perspective.

Because the field of catalysis is one where current activity is enormous and because various topics in catalysis reach a degree of maturity at different points in time, it is not

expedient to impose a preconceived ordered structure upon *Catalysis: Science and Technology* with each volume devoted to a particular subject area. Instead, each topic is dealt with when it is most appropriate to do so. It will be sufficient if the entire subject has been properly covered by the time the last volume in the series appears. Nevertheless, the Editors will try to organize the subject matter so as to minimize unnecessary duplication between chapters, and to impose a reasonable uniformity of style and approach. Ultimately, these aspects of the presentation of this work must remain the responsibility of the Editors, rather than of individual authors.

The Editors would like to take this opportunity to give their sincere thanks to all the authors whose labors make this reference work possible. However, we all stand in debt to the numerous scientists and engineers whose efforts have built the discipline of catalysis into what it is today: we can do no more than dedicate these volumes to them.

Preface

NMR methods have for a considerable time been standard processes for the analysis of molecular structure: so much so that they are now universally regarded as indispensable for this purpose. Nevertheless, with the passage of time, NMR methodology has been elaborated to levels of ever increasing complexity and analytical sophistication so that the non-specialist may now be readily excused for the belief that for anything beyond relatively elementary methods one would be well advised to work in collaboration with the specialist experts.

The application of NMR methods to the field of catalysis occurred, in the main, relatively late in the day, mainly because those catalysts of greatest industrial importance, that is heterogeneous catalysts, are solids and so require special NMR methods if usefully narrow NMR lines are to be observable. Even so, magic-angle spinning NMR methodology is now thoroughly well established and is finding increasing use in the study of catalyst structure. Of course, conventional NMR methods have been used for a considerable time for the analysis of the products of catalytic reactions.

Chapter 1 of the present volume by Professor Jacques Fraissard and his collaborators is designed to give an account of the application of NMR methods to the field of catalysis, but not including the conventional use of NMR for reaction product analysis, since this is already well covered in the existing NMR literature.

The fact is that those who wish to use NMR methods will receive the greatest reward if they approach the subject with a reasonable grounding in the theory, and for this reason Chapter 1 gives an introduction to the more important aspects of NMR theory, in the light of which the later parts of the Chapter are to be viewed. Following this theoretical

introduction. Chapter 1 proceeds to a discussion of various specific applications, including the study of adsorbed molecules, the structure of important classes of catalysts by NMR methods using nuclei such as ^{29}Si , ^{27}Al and ^{51}V , the use of NMR methods for studying the acidity of solids, the NMR of physisorbed ^{129}Xe for the study of catalyst structure, the use of ^{195}Pt NMR for the structure of platinum catalysts, and the use of NMR methods (via line width) for estimating molecular mobility, thus addressing the question of molecular diffusion in catalysts.

Our aim is thus to provide those who work in the field of catalytic science and technology with an account of NMR methods which should prove of relevance to their problems, together with a summary of the existing literature in the light of which the likely application of various NMR methods to future problems may be judged.

Since the present volume is the penultimate one in the series, the opportunity has been taken in Chapter 2 to provide a glossary which gives the meaning of the more commonly used special terms used in catalytic science and technology. Established practitioners in the field will probably find little of novelty here, but the compilation will hopefully be of value to non-specialists coming to the field for the first time.

List of Contributors

Professor J. Fraissard
Professor R. Vincent
Professor C. Doremieux
Laboratoire de Chimie des Surfaces
CNRS URA 1428
Université Pierre et Marie Curie
4 Place Jussieu
75252 Paris Cedex 05, France

Professor J. Karger
Professor H. Pfeiffer
Fachbereich Physik
Universität Leipzig
Linnéstrasse 5
04103 Leipzig, Germany

Professor J.L. Falconer
Department of Chemical Engineering
University of Colorado
Campus Box 424
Boulder, CO 80309, USA

Chapter 1

Application of NMR Methods to Catalysis

Jacques Fraissard¹,

with associate authors

Robert Vincent¹, Claudine Doremieux¹,

Jörg Kärger², Harry Pfeifer²

¹ Laboratoire de Chimie des Surfaces, CNRS URA 1428, Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris Cedex 05, France

² Fachbereich Physik, Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany

Contents

1. Introduction	3
2. Introduction to Theory of Solid State NMR	5
A. Nuclear Spin Interactions in a Solid	5
1. Zeeman Interaction: \hat{H}_Z	6
Population of levels	7
2. Interaction with the Radiofrequency Field: \hat{H}_{RF}	9
a. Continuous Wave NMR	10
b. Pulsed NMR	13
3. Dipolar Interaction: \hat{H}_D	13
a. Static Part. Term \hat{A}	14
b. Oscillating Part. Term \hat{B}	14
c. Effect of Dipolar Coupling on Two Isolated Spin 1/2 Nuclei	15
4. Quadrupolar Interaction: \hat{H}_Q	17
5. Chemical Shift Interaction: \hat{H}_{CS}	21
6. J-Coupling: \hat{H}_J (Indirect Nuclear-Nuclear Interactions)	22
7. The Effect of Unpaired Electrons	24
a. Anisotropic Dipolar Coupling	25
b. Isotropic or Contact Interaction	25
c. Knight Shift and Korringa Relation	26
B. Methods Particular to Solid State NMR	27
1. Heteronuclear Decoupling	27
2. Cross-Polarization	27
3. Magic Angle Spinning (MAS)	32
4. Multiple Pulse Sequences	33
3. NMR Techniques for the Study of Adsorbed Molecules	34
A. Introduction	34
B. Experimental Conditions and Difficulties	35
1. Sensitivity	35
2. Overhauser Effect (NOE)	36
C. Measurement of Resonance Shifts	36
Chemical Shift Measurement: Choice of a Reference: Liquid or Solid State	38
D. Broadening and Magnetic Shielding Anisotropy	38
E. Exchange Effects	39
1. First Method	41
2. Second Method	41
4. High Resolution NMR of Heavy Nuclei	42
A. Introduction	42
B. ²⁹ Si-NMR of Silicates	42

C. ^{29}Si -NMR of Zeolites	44
1. Distribution of the Si and Al Atoms	45
2. Si/Al Ratio in the Framework	47
3. Crystallographic T-Sites	49
4. Influence of the TOT Bond Angle	49
5. Dealumination of Zeolites	49
6. Zeolite Synthesis	50
D. ^{27}Al -NMR of Zeolites	52
1. Structure	54
2. Dealumination and Coking	55
3. Nutation NMR	57
E. Other Heavy Nuclei	59
1. ^{13}C -NMR	59
a. Templates and Crystallization of Zeolites	59
b. Chemisorbed Phases	62
2. ^{51}V -NMR	62
5. High Resolution NMR and the Acidity of Solids	63
A. HR ^1H -NMR	63
1. Introduction	63
2. Experimental Techniques and Difficulties	65
3. Fast Exchange	66
4. Effect of Hydrogen Bonding	68
a. Anisotropic Chemical Shift	68
b. Isotropic Chemical Shift	68
5. Results Concerning the Acidity Dependence of δ_{iso}	69
B. HR NMR of Nuclei Other than ^1H	74
1. Direct Study of Surface Properties	74
2. Study of Acidity by NMR of Adsorbed Molecules	76
a. ^{13}C -NMR	76
b. ^{15}N -NMR	79
c. ^{13}C and ^{15}N -NMR	81
d. ^{29}Si -NMR	82
e. ^{29}Si and ^{13}C -NMR	86
f. ^{31}P -MAS-NMR	86
C. Conclusions	87
6. Space Distribution of Protons in Rigid Lattice Conditions: Acidity of Solids	88
A. Introduction	88
B. The Method of Moments	88
C. Line-Shape Analysis	90
D. Spectrum Simulation from Miscellaneous Models	91
E. Study of the Superficial Constitutive Water of Titania	94
F. Study of the Acidity of Zeolites	99
G. Conclusions	103
7. NMR of Physisorbed Molecules Used as Probes (^{129}Xe)	103
A. Generalities	104
B. Influence of Structure	104
C. Mixtures, Crystallinity, and Pore Blocking	108
D. Influence of Cations	111
1. Diamagnetic Cations	111
2. Paramagnetic Cations	114
E. Dealumination of HY Zeolite. Deactivation by Coking	115
F. Conclusions	117
8. Supported Metal and Paramagnetic Catalysts	119
A. Introduction	119
B. ^1H -NMR Study of Hydrogen Chemisorbed on Metals: Application to Dispersion	119
1. Hydrogen Chemisorbed on Platinum	120
2. Hydrogen Sorption on Palladium	123
C. ^{129}Xe -NMR of Adsorbed Xenon for Studying Metal-Zeolites	127
1. Generalities-Models	127
2. Chemisorption of Hydrogen: Determination of Particle Size	129
3. Chemisorption of Other Gases	132
4. Conclusions	133

D. ^{195}Pt -NMR Studies of Platinum Catalysts	133
1. Generalities	133
Knight Shift	134
2. Experiments: Spin-Echo Technique	135
3. Results	136
a. Untreated Samples	136
b. Effect of Chemical Treatment of the "Surface Peak"	137
c. SEDOR Technique	137
d. The Bonding of Molecules to the Metal	140
4. Application to Catalysis	146
E. Paramagnetic Systems	148
1. Adsorption of Olefines on Paramagnetic Centers	148
2. Decomposition of Formic Acid on Electron-Donor Centers	149
9. Molecular Mobility	154
A. The Elementary Steps of Molecular Migration	154
B. Intracrystalline Self-Diffusion	159
C. Tracer Desorption	163
D. Long-Range Self-Diffusion	166
10. References	168

1. Introduction

The aim of this Section is to give a brief historical account of NMR spectroscopy and to present the various sections of this work.

The NMR phenomenon was discovered in 1946 and very rapidly became one of the most powerful tools for the elucidation of molecular structure and dynamics, particularly in organic chemistry. NMR spectroscopy consists of inducing transitions between magnetic levels of nuclear spins differentiated by the application of a magnetic field. The transition frequency corresponding to a nucleus in a given chemical environment is a particularly sensitive probe of the latter. If the transition of nuclei of a given element in different environments can be resolved, precise unambiguous information about the structure, the conformation and the molecular motion of the system can be obtained. The corresponding spectrum is then referred to as "high resolution, HR".

From 1950–1970, HR-NMR studies were mainly concerned with liquids since effects of certain nuclear interactions, which can cause excessive broadening, are averaged to zero or to discrete isotropic values due to the rapid random motion of the molecules. During this period, particularly rich for NMR theory, most studies were related, for reasons of sensitivity, to nuclei which were abundant and easily detected (H, F, P...). In the last 10 years, superconducting high field, and especially, Fourier transform techniques have made it possible to observe nuclei of low abundance and/or low detection sensitivity, (for example some isotopes of C, Si, etc.).

The application of NMR to solids during this period was very limited. The main reason is that in rigid systems (solids, but also very strongly chemisorbed molecules) the interaction which can cause considerable broadening of the signals cannot be averaged to a small value by the motion of the species.

The potential of NMR spectroscopy is however such that it was unthinkable not to use such a tool to study rigid systems. The result has been the development, since about 1970, of sophisticated experimental techniques for signal narrowing

Contents

<i>Chapter 1</i>	Application of NMR Methods to Catalysis (<i>J. Fraissard, R. Vincent, C. Doremieux, J. Karger, and H. Pfeiffer</i>)	1
<i>Chapter 2</i>	Glossary of Terminology Used in Catalysis (<i>J. L. Falconer</i>)	177
<i>Subject Index</i>	211
<i>Author Index Volumes 1-10</i>	215

Chapter 1

Application of NMR Methods to Catalysis

Jacques Fraissard¹,

with associate authors

Robert Vincent¹, Claudine Doremieux¹,

Jörg Kärger², Harry Pfeifer²

¹Laboratoire de Chimie des Surfaces, CNRS URA 1428, Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris Cedex 05, France

²Fachbereich Physik, Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany

Contents

1. Introduction	3
2. Introduction to Theory of Solid State NMR	5
A. Nuclear Spin Interactions in a Solid	5
1. Zeeman Interaction: \hat{H}_Z	6
Population of levels	7
2. Interaction with the Radiofrequency Field: \hat{H}_{RF}	9
a. Continuous Wave NMR	10
b. Pulsed NMR	13
3. Dipolar Interaction: \hat{H}_D	13
a. Static Part. Term \hat{A}	14
b. Oscillating Part. Term \hat{B}	14
c. Effect of Dipolar Coupling on Two Isolated Spin 1/2 Nuclei	15
4. Quadrupolar Interaction: \hat{H}_Q	17
5. Chemical Shift Interaction: \hat{H}_{CS}	21
6. J-Coupling: \hat{H}_J (Indirect Nuclear-Nuclear Interactions)	22
7. The Effect of Unpaired Electrons	24
a. Anisotropic Dipolar Coupling	25
b. Isotropic or Contact Interaction	25
c. Knight Shift and Korringa Relation	26
B. Methods Particular to Solid State NMR	27
1. Heteronuclear Decoupling	27
2. Cross-Polarization	27
3. Magic Angle Spinning (MAS)	32
4. Multiple Pulse Sequences	33
3. NMR Techniques for the Study of Adsorbed Molecules	34
A. Introduction	34
B. Experimental Conditions and Difficulties	35
1. Sensitivity	35
2. Overhauser Effect (NOE)	36
C. Measurement of Resonance Shifts	36
Chemical Shift Measurement: Choice of a Reference: Liquid or Solid State	38
D. Broadening and Magnetic Shielding Anisotropy	38
E. Exchange Effects	39
1. First Method	41
2. Second Method	41
4. High Resolution NMR of Heavy Nuclei	42
A. Introduction	42
B. ²⁹ Si-NMR of Silicates	42

C.	^{29}Si -NMR of Zeolites	44
1.	Distribution of the Si and Al Atoms	45
2.	Si Al Ratio in the Framework	47
3.	Crystallographic T-Sites	49
4.	Influence of the TOT Bond Angle	49
5.	Dealumination of Zeolites	49
6.	Zeolite Synthesis	50
D.	^{27}Al -NMR of Zeolites	52
1.	Structure	54
2.	Dealumination and Coking	55
3.	Nutation NMR	57
E.	Other Heavy Nuclei	59
1.	^{13}C -NMR	59
a.	Templates and Crystallization of Zeolites	59
b.	Chemisorbed Phases	62
2.	^{51}V -NMR	62
5.	High Resolution NMR and the Acidity of Solids	63
A.	HR ^1H -NMR	63
1.	Introduction	63
2.	Experimental Techniques and Difficulties	65
3.	Fast Exchange	66
4.	Effect of Hydrogen Bonding	68
a.	Anisotropic Chemical Shift	68
b.	Isotropic Chemical Shift	68
5.	Results Concerning the Acidity Dependence of δ_{iso}	69
B.	HR NMR of Nuclei Other than ^1H	74
1.	Direct Study of Surface Properties	74
2.	Study of Acidity by NMR of Adsorbed Molecules	76
a.	^{13}C -NMR	76
b.	^{15}N -NMR	79
c.	^{13}C and ^{15}N -NMR	81
d.	^{29}Si -NMR	82
e.	^{29}Si and ^{13}C -NMR	86
f.	^{31}P -MAS-NMR	86
C.	Conclusions	87
6.	Space Distribution of Protons in Rigid Lattice Conditions: Acidity of Solids	88
A.	Introduction	88
B.	The Method of Moments	88
C.	Line-Shape Analysis	90
D.	Spectrum Simulation from Miscellaneous Models	91
E.	Study of the Superficial Constitutive Water of Titania	94
F.	Study of the Acidity of Zeolites	99
G.	Conclusions	103
7.	NMR of Physisorbed Molecules Used as Probes (^{129}Xe)	103
A.	Generalities	104
B.	Influence of Structure	104
C.	Mixtures, Crystallinity, and Pore Blocking	108
D.	Influence of Cations	111
1.	Diamagnetic Cations	111
2.	Paramagnetic Cations	114
E.	Dealumination of HY Zeolite. Deactivation by Coking	115
F.	Conclusions	117
8.	Supported Metal and Paramagnetic Catalysts	119
A.	Introduction	119
B.	^1H -NMR Study of Hydrogen Chemisorbed on Metals: Application to Dispersion	119
1.	Hydrogen Chemisorbed on Platinum	120
2.	Hydrogen Sorption on Palladium	123
C.	^{129}Xe -NMR of Adsorbed Xenon for Studying Metal-Zeolites	127
1.	Generalities-Models	127
2.	Chemisorption of Hydrogen: Determination of Particle Size	129
3.	Chemisorption of Other Gases	132
4.	Conclusions	133

D. ^{195}Pt -NMR Studies of Platinum Catalysts	133
1. Generalities	133
Knight Shift	134
2. Experiments: Spin-Echo Technique	135
3. Results	136
a. Untreated Samples	136
b. Effect of Chemical Treatment of the "Surface Peak"	137
c. SEDOR Technique	137
d. The Bonding of Molecules to the Metal	140
4. Application to Catalysis	146
E. Paramagnetic Systems	148
1. Adsorption of Olefines on Paramagnetic Centers	148
2. Decomposition of Formic Acid on Electron-Donor Centers	149
9. Molecular Mobility	154
A. The Elementary Steps of Molecular Migration	154
B. Intracrystalline Self-Diffusion	159
C. Tracer Desorption	163
D. Long-Range Self-Diffusion	166
10. References	168

1. Introduction

The aim of this Section is to give a brief historical account of NMR spectroscopy and to present the various sections of this work.

The NMR phenomenon was discovered in 1946 and very rapidly became one of the most powerful tools for the elucidation of molecular structure and dynamics, particularly in organic chemistry. NMR spectroscopy consists of inducing transitions between magnetic levels of nuclear spins differentiated by the application of a magnetic field. The transition frequency corresponding to a nucleus in a given chemical environment is a particularly sensitive probe of the latter. If the transition of nuclei of a given element in different environments can be resolved, precise unambiguous information about the structure, the conformation and the molecular motion of the system can be obtained. The corresponding spectrum is then referred to as "high resolution, HR".

From 1950–1970, HR-NMR studies were mainly concerned with liquids since effects of certain nuclear interactions, which can cause excessive broadening, are averaged to zero or to discrete isotropic values due to the rapid random motion of the molecules. During this period, particularly rich for NMR theory, most studies were related, for reasons of sensitivity, to nuclei which were abundant and easily detected (H, F, P...). In the last 10 years, superconducting high field, and especially, Fourier transform techniques have made it possible to observe nuclei of low abundance and/or low detection sensitivity, (for example some isotopes of C, Si, etc.).

The application of NMR to solids during this period was very limited. The main reason is that in rigid systems (solids, but also very strongly chemisorbed molecules) the interaction which can cause considerable broadening of the signals cannot be averaged to a small value by the motion of the species.

The potential of NMR spectroscopy is however such that it was unthinkable not to use such a tool to study rigid systems. The result has been the development, since about 1970, of sophisticated experimental techniques for signal narrowing

so as to obtain spectral resolution similar to that for liquids. These are principally: magic angle spinning (MAS); high-power dipolar coupling and appropriate multipulse sequences. In addition, the cross-polarization (CP) technique was developed to overcome the problem of low sensitivity in the solid state NMR of nuclei of low abundance (^{13}C , ^{29}Si , etc.). A comprehensive survey of the various experimental techniques available in multinuclear solid state NMR, the information which can be deduced from the spectra in each case, and a very large range of applications in various fields, can be found in the excellent books of Fyfe [1] and Gerstein and Dybowski [2], while Abragam [3] discusses principles.

In a comprehensive study of a solid adsorbent acting as catalyst in interaction with adsorbed molecules, different aspects should be included:

- The study of the adsorbent itself;
- The identification of the active surface sites in the presence of adsorbed molecules;
- The state of adsorbed molecules at different temperatures;
- The study of catalytic transformations at the solid surface;
- Finally the mobility of the protons, counterions and adsorbed species at the surface.

In this work we shall not give an exhaustive review of all the NMR studies performed in the field of solid catalysts (surface properties, chemisorption and reaction mechanisms). We shall simply show through a few selected examples the interest of studying the various interactions to which nuclear spins are submitted as a means of resolving certain problems of heterogeneous catalysis.

Section 2 gives a short review of the physical background of the main types of nuclear magnetic interactions affecting the NMR spectra of solids, and of the various experimental techniques applied in NMR studies of solids.

Section 3 completes the previous one with a specific study of adsorbed species.

These sections are intended merely to make it easier to understand the applications described thereafter without having to refer continuously to textbooks. We would point out that certain experimental details will be given in the examples rather than in these sections.

Section 4 concerns the use of broad-line NMR in the study of rigid lattices (systems in which the motion of the chemical species is severely reduced). The spectrum then usually depends on the dipolar interactions which are directly related to the distances between nuclear spins and, therefore, between the atoms. We discuss various applications to the study of proton distribution on solid surfaces (structure, heterogeneous-equilibria, acidity).

Chemical shifts of quasi-rigid chemical species can be determined if the signal can be narrowed either by the above mentioned HR-NMR techniques or by increasing the motion of the species. This is the case, for example, of chemisorbed phases. In section 5 we show how the adsorption of bases can be used to induce the motion of acidic hydrogens of solids and to determine their chemical shifts indirectly. We show also the interest of MAS-NMR for the study of the acidity of solid catalysts.

Section 6 deals with the study of the structure of solids by all HR-NMR techniques. We shall mainly discuss the study of zeolites (^{29}Si , ^{27}Al).