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BOOK REVIEWS

NMR Techniques in Catalysis. Edited by Alexis T. Bell and Alexander Pines. Dekker, New York, 1994. 432 pp. $165.00.

This book is a comprehensive presentation of state-of-the-art nuclear magnetic resonance (NMR) techniques applied to the study of industrially relevant catalysts and catalytic processes. The editors and authors have woven the principles of solid state NMR and new solid state NMR experiments into the discussion of NMR results for many catalyst systems. The ability of NMR to elucidate atomic level structure and dynamics is shown in each of the seven chapters. Authors describe one- and two-dimensional solid state NMR experiments which reveal the bond connectivities of nuclei in catalysts, as well as the distances between them. Other experiments are used to determine the distribution of observable nuclei in or on the catalyst. The chemical nature of each observable nucleus is revealed in its chemical shift tensor or its quadrupole tensor. The motion of the molecules which contain the observed nuclei is revealed by a variety of techniques, including pulsed magnetic field gradient NMR. *In situ* variable temperature solid state NMR is shown to reveal the chemistry of catalysis as it actually occurs. Other NMR methods are available for the characterization of acid and base sites on catalysts. In all chapters there is extensive discussion of a wide range of different catalysts and reactions. This book is recommended reading for all who study catalysis and for all who use solid state NMR spectroscopy.

The book is divided into seven chapters, with each chapter focusing on a different type of catalyst or NMR spectroscopy. The first chapter, by Fyfe *et al.* gives an extremely useful overview of the NMR of zeolites and related materials. ^{29}Si is a spin 1/2 nucleus and therefore is amenable to familiar solid state techniques such as magic angle spinning (MAS) and cross polarization magic angle spinning (CPMAS). The authors discuss the relation between the chemical shift of ^{29}Si and the substituents on the silicon atom. Two-dimensional (2D) homonuclear ^{29}Si NMR spectra based on the scalar J coupling (COSY and INADEQUATE) are used to elucidate bond connectivities for several zeolites. MAS spectra obtained for ^{27}Al and ^{17}O illustrate the effect of coordination and chemistry on the quadrupole tensor and on the chemical shift. Dynamic angle spinning (DAS) and double rotation (DOR) NMR are shown to produce narrow lines for the ^{27}Al and ^{17}O central transitions, thereby making it possible to resolve different resonances with the same coordination. Heteronuclear through-space distance information due to the dipolar interaction is demonstrated in $^{31}P \leftrightarrow {}^{27}Al$ 1D CPMAS results for $AlPO_4$ and a heteronuclear 2D $^{27}Al \rightarrow {}^{31}P$ correlation of the same material.

Chapter 2, by Karger and Pfeifer, provides an excellent review of NMR techniques for the elucidation of molecular diffusion in catalysts. Techniques such as NMR tracer exchange and NMR microimaging can be used to monitor the concentration and distribution of adsorbates as a function of time. ^{129}Xe NMR yields information about the pore and channel dimensions within the catalyst, as well as information about adsorbed molecules. ^{1}H spin-lattice relaxation measurements are shown to yield the mean time between successive translation jumps of adsorbed molecules if paramagnetic impurities are present in the catalyst and the conditions are right. ^{2}H lineshape analysis is also shown to be useful in the characterization of the reorientation experience by adsorbed deuterated species. The bulk of the chapter, however, discusses the application of pulsed field gradient (PFG) NMR for the determination of modes of translational diffusion in catalyst samples. PFG NMR is shown to be useful for determining intercrystalline, intracrystalline, single file, and long-range diffusion coefficients, as well as the dependence of diffusion on the anisotropy of the sample and on concentrations of single and multiple components adsorbed in the catalyst.

In situ NMR of catalytic reactions, as explained in the third chapter by Haw, is NMR spectroscopy of samples which have been prepared in such a way that the characteristics of industrial catalysis are reproduced as closely as possible. Several useful methods are described for preparing such samples. Variable temperature *in situ* studies involving ^{13}C, ^{1}H, ^{77}Se, and ^{133}Cs NMR (mostly MAS and CPMAS ^{13}C) are reported for labeled and unlabeled reactants on H-ZSM5 and ZSM5 zeolite catalysts. The spectra reveal not only the expected reactants and products but also a variety of unusual species formed at catalytic temperatures, among them carbenium cations and trimethyloxonium cations.

Chapter 4, by Eckert, deals with the NMR of bulk oxide catalysts. The catalytic activity of these catalysts depends on two basic properties of the oxide surface, redox activity, which enables hydrogen abstraction from or oxygen transfer to adsorbed molecules, and acid–base character, which enables catalytic cracking and isomerization of adsorbed molecules. Solid state NMR techniques such as static (wideline) NMR, multinuclear MAS NMR, quadrupolar nutation NMR, and CPMAS NMR are discussed. The results from these experiments are presented for a wide variety of catalysts and nuclei. Both this chapter and Chapter 5 discuss NMR results for transitional aluminas. ^{27}Al MAS NMR can easily differentiate between octahedral and tetrahedral aluminum coordination. ^{27}Al resonances from Brønsted acid sites have been observed by cross polarization from surface hydroxyl hydrogens in CPMAS experiments, and ^{27}Al resonances for Lewis acid sites have been observed by cross polarization from adsorbed pyridine.

Written by Maciel and Ellis, Chapter 5 focuses exclusively on the NMR characterization of silica and alumina surfaces. The goal of surface characterization is the preferential polarization of surface nuclei or nuclei in adsorbed species. For example, $^{1}H \rightarrow {}^{29}Si$ CPMAS experiments have been used since 1980 to characterize silica surfaces. Surface silanols provide the ^{1}H source for cross polarization in the absence of adsorbed species, and the resulting spectra reveal distinct Q_2, Q_3, and Q_4 ^{29}Si resonances. $^{1}H \rightarrow {}^{27}Al$ and $^{1}H \rightarrow {}^{17}O$ cross polarization of aluminas and silicas is also discussed. The Hartmann–Hahn match condition is different for these quadrupolar nuclei than for $I = \frac{1}{2}$ nuclei, as is the maximum polarization possible from the limited number of protons. Two kinds of proton source are used in the spectra shown, in one case surface hydroxyls and in the other case adsorbed pyridine. The former reveals two types of Brønsted acid sites, octahedral O_h and tetrahedral T_d. The latter reveals Lewis acid sites on partially dehydrated alumina. ^{1}H NMR is also discussed as a surface characterization method. Results from single-pulse MAS experiments and combined rotation and multiple-pulse spectroscopy (CRAMPS) are shown. In the case of silica–aluminas, for example, the spectra reveal a resonance at 7 ppm that does not appear in spectra of silica or alumina alone. This resonance is assigned to bridging hydroxyls between silica and alumina and may be responsible for acid catalysis in a variety of industrial processes. This chapter also presents multinuclear studies of modified silicas and alumi-

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nas. ^{29}Si, ^{13}C, ^{31}P, ^{87}Rb, ^{133}Cs, and ^{95}Mo spectra are analyzed for several catalytic systems.

Chapter 6 deals with a class of catalysts which has been less extensively explored with NMR, namely layered materials such as clays and pillared clays, zirconium phosphates, aluminophosphates, layered metal sulfides, and graphite. The authors, Haddix and Narayana, give a brief review of clay structures and pillared clays, then go on to review ^{29}Si and ^{27}Al solid state NMR results for these materials. The emphasis is on structural findings. Multinuclear NMR results for a variety of cations adsorbed or trapped in clays are reported. Effects of organic adsorbates are discussed, both in terms of the NMR spectra of the adsorbate and in terms of the NMR spectra of the clay. ^{31}P MAS NMR spectra of zirconium phosphates show clear differences among the various thermodynamic phases of the material. Variable temperature studies of $ZrPO_4$ gels from room temperature to 1473 K show dehydration to form ZrP_2O_7.

The last chapter, by Kolodziejski and Klinowski, reviews new solid state NMR techniques for the study of catalysis, although many of the same techniques are described in earlier chapters. It is extremely useful because it concisely summarizes the advantages and limitations of the new techniques, but does not get bogged down in jargon or unnecessary details. Techniques based on J coupling, such as the two-dimensional COSY and INADEQUATE experiments, are discussed first. These give information about bonding connectivities between observed nuclei. Next, many techniques based on dipolar coupling are treated. The goal of most of these methods is to obtain information about through-space interatomic distances or spin diffusion. Spectra from two-dimensional homonuclear ^{13}C and ^{31}P spin diffusion experiments are presented, as are the conditions necessary for useful results. One-dimensional rotational resonance NMR spectroscopy is also described, as is the additional information necessary to calculate internuclear distances. Multiple-quantum (MQ) 2D NMR is shown to be useful for the characterization of the distribution of spins in solids. The SEDOR, REDOR, and TEDOR experiments are discussed, and all are demonstrated to be useful for the determination of dipolar connectivities and internuclear distances. Cross polarization of odd half-integer quadrupolar nuclei like ^{27}Al, ^{17}O, and ^{11}B can be used for the same purpose. Several examples of such spectra are shown. New techniques for quadrupolar nuclei are discussed next. Quadrupolar nutation is a 2D experiment that allows one to determine if a resonance represents the full manifold of quadrupolar transitions or if only the central transition is observed. If two nuclei of the same isotope differ significantly with respect to their quadrupole couplings, they can be resolved with quadrupolar nutation. DAS and DOR NMR techniques provide 2D and 1D methods, respectively, for obtaining high-resolution quadrupolar NMR spectra for central transitions. Some beautiful ^{27}Al DOR spectra are shown for dehydrated and partially rehydrated VPI-5. Finally, there are brief discussions of several interesting new techniques. NMR images of catalysts are presented. Optically pumped ^{129}Xe and the Pasadena effect are demonstrated as means by which adsorbed molecules or the surface itself can be polarized. Mechanical detection of NMR signals in a magnetic force microscope is also possible, although the only examples so far are for electron spin resonance.

The book contains beautiful spectra, informative figures, and a good index. The text is mainly descriptive. The reader is not overwhelmed with extensive mathematical treatments, although important equations and relationships are provided.

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Surface Chemistry and Catalysis. Gabor A. Somorjai. Wiley, New York, 1994. 667 pp.

In an era when scientific books written by a single author are few and far between, the third such book by a coryphaeus of surface science is an event that deserves the attention of those who teach surface chemistry or work in heterogeneous catalysis. The mere size of the book should not deter the student, who will find 100 problems among eight chapters with solutions to 58 of them. Further, more than 300 pages consist of tables of surface structures, kinetic parameters, and 3324 references with full titles, a data bank large enough to guide the most dedicated researcher through the forest of contemporary chemistry on solid surfaces.

The reader interested in quality, not quantity, will find one superb chapter that depicts the monumental work of the author who, over the years, has been one of the main architects of a cathedral dedicated to the structure of surfaces. Like so many of the ancient cathedrals, this one is also unfinished but it is beautiful, in the sense of Thomas Aquinas, who defined beauty as splendor ordinis, the splendor of order. Another chapter that reflects the many contributions of Gabor Somorjai deals with the surface chemical bond. Going back to the first chapter, I find it eminently useful as an introduction to the subject, including 58 definitions of acronyms, the basic jargon of the arsenal of surface science techniques. In addition, the first chapter will motivate the student with pictures of an integrated microelectronic circuit, a human brain, and the spine of a sea urchin. Similarly, the beginner will be fascinated by the last chapter of the book on mechanical properties of surfaces, including hardness, adhesion, tribology, lubrication, coatings, and fracture.

The breadth and depth of coverage by a single author are well illustrated by an excellent chapter on electrical properties of surfaces with many of the important electron spectroscopic techniques for surface analysis. Two more chapters introducing surface thermodynamics and dynamics (i.e., kinetics) are qualitatively adequate but quantitatively unsatisfactory to this reviewer. Indeed, the student receives only half of the message from an emphasis on energy, with entropy only folded into free energy. Yet entropy is too important to be slighted with only one entry in the comprehensive subject index. For example, Gabor Somorjai's 1981 book, "Chemistry in Two Dimensions: Surfaces," coined in its title an expression that has often been quoted. What is the difference between chemistry in two or three dimensions? The important feature of the chemistry of solid surfaces is the existence of Langmuir distinguishable sites occupied by adsorbates without appreciable surface diffusion during the observation time of the pertinent surface chemistry. When adsorption is localized on Langmuir sites, the surface chemical potential of the adsorbate includes a term, the configuration entropy, that actually accounts for the form of the Langmuir adsorption isotherm. This statistical mechanical way of looking at Langmuir's isotherm, as first done by Everett in 1950, reveals the special feature of the chemistry in two dimensions on a Langmuir surface. Another advantage of entropy is that it can often be calculated or estimated, while energy remains much less accessible.

The last chapter remaining to be reviewed here deals with catalysis by surfaces. The work in Professor Somorjai's laboratory, where areal rates of catalytic reactions on large single crystals of metals *at high pressures* were first measured, must be considered in my opinion as a breakthrough advance in surface catalysis. Since the work of the Somorjai group, such data were also obtained in many other laboratories for many reactions on many single crystals of many different metals. They can be compared with data obtained on conventional high specific surface area samples. These comparisons have transformed heterogeneous catalysis to a quantitative field of surface chemistry, i.e., a science. The striking data on ammonia synthesis on iron single crystals, first obtained in the Somorjai laboratories, established unequivocally