

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

the previously suspected structure sensitivity or crystalline surface anisotropy of that reaction, or of any reaction for that matter.

Considering the importance of that work, it is perhaps understandable that this reviewer was disappointed by the chapter on catalysis. On that note, which detracts in no way from the tour de force of Gabor Somorjai's latest (but we hope not the last) book, it is possible to add the teasing if not pedantic note that is the only reward for the delicate task of writing a review. On page 305, the author states that the success of Langmuir's treatment is "due to the relative insensitivity of macroscopic adsorption measurement to the atomic details of the adsorption process." Such hand waving is not acceptable today in view of the quantitative work done by Gabor Somorjai and many other surface scientists over the past 30 years. Thanks to that work, humility is no longer required in catalysis science except in the sense that a true scientist is always humble when talking about his or her own work.

Anyone working in surface science or catalysis science needs a desk copy of Somorjai's latest book.

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New Aspects of Spillover Effect in Catalysis. Edited by T. Inui, K. Fujimoto, T. Uchijima, and M. Masai. *Studies in Surface and Catalysis, Vol. 77.* Elsevier, Amsterdam, 1993. 435 pp.

The Third International Conference on Spillover was held in Kyoto, Japan, August 17–20, 1993. This book contains the proceedings from this meeting.

The First International Symposium on Spillover of adsorbed species took place in 1983 in Lyons, France. Spillover was found to encompass not only adsorption but gasification of solids, creation of catalytically active sites, and reaction with adsorbed species. The Second International Symposium on Spillover was held in Leipzig in 1989. Additional insights into the spillover of nonhydrogen species, the mechanism and rate of spillover and surface diffusion, and the potential involvement of spillover in applied catalysis were discussed.

The Third International Symposium on Spillover was held in Kyoto in 1993. The focus of the presentations was on the broad extent of the applications of spillover in applied catalysis and the design of catalysts based on the phenomena associated with spillover. It was also apparent that many species were involved in spillover and that, even for a single molecule, different fragments, which also could be in various forms (charged, uncharged, or radical), could be involved in spillover. Indeed, many reactions on catalysts comprising multiple phases were discussed, as was the evidence that spillover might participate in the catal-

ysis. The spillover could be involved during activation or reaction, or to prevent deactivation.

The first several papers in this book discuss several crucial aspects of spillover and are a worthy start for anyone working in heterogeneous catalysis where spillover may contribute. These include extensive perspectives on spillover by Teichner (pp. 27–43). Pajonk (pp. 85–94) discusses the many studies which have attempted to characterize the nature of the spillover species and Conner discusses the spectroscopic insight into spillover (pp. 61–68). Another paper summarizes the contributions of spillover to catalysis primarily for methanol synthesis and supported MoS₂ catalysts (Barrett *et al.* pp. 207–212). Delmon (pp. 1–8) elucidates the concept of remote control of catalytic activity by spillover species. The impact of spillover on industrial catalysts is discussed by Fujimoto (pp. 9–16), Inui (pp. 17–26), and Moro-oka (pp. 95–104, for oxygen spillover). The relationship between spillover and catalytic acidity is detailed in an interesting series of papers by Kikuchi and Matsuda (pp. 53–60), Hattori (pp. 69–76), and Nakamura *et al.* (pp. 77–84).

Over 20 other oral papers were presented and many describe more recent findings of spillover in catalytic reactions. These include hydrogen spillover in bimetallics (On *et al.*, pp. 125–130), reversible and irreversible spillover in reforming (Chen *et al.*, pp. 131–136), spillover in oxygenate hydrogenation (Chen and Falconer, pp. 171–176), spillover in membranes (Eguchi *et al.*, pp. 195–201), oxygen spillover in Pt/CeO₂ (Li *et al.*, pp. 217–222), conductivity changes due to spillover (Braunschweig *et al.*, pp. 183–187) observations by photoemission and field ion microscopies (Block *et al.*, pp. 189–194), and methoxy formation during syngas reaction on Pd/Al₂O₃ detected by ¹³C and ¹H NMR (Han *et al.*, pp. 223–228). Forty posters are also included in these proceedings, many suggesting unique applications of spillover.

This book brings up to date the most recent aspects of spillover and truly broadens the areas where spillover is proposed to have an influence. The speculations and data which implicate spillover in a broad series of applied catalysis are intriguing and are worthy of further study. Teichner hypothesizes (p. 39) that there is "a very high probability... [that] spillover does already exist in the mechanism of most catalytic reactions or may be introduced by a new design of catalysts." The book does, however, represent a compendium of studies by those who believe that spillover does or may have a significant impact in catalysis. A certain bias is therefore reflected in many of the papers and the arguments in favor of other explanations are not always discussed in detail. However, with this in mind, this book is crucial background for anyone who comes to conclude that a species formed on one surface may spillover onto another surface (or part of the surface where it does not adsorb directly) on which it may react with the surface or other adsorbed species.

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