NMR Techniques in Catalysis

NMR TECHNIQUES IN CATALYSIS

edited by

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Preface

Modern chemical processes and petroleum refining are critically dependent on the use of solid catalysts to achieve desirable selectivities and rates of product formation. In order to understand the function of such heterogeneous catalysts and to optimize their performance, it is essential to characterize the structure of catalytic materials and surfaces, to understand the interactions between molecules and catalysts, and to follow the dynamics of diffusion and chemical reactions of molecules during the course of catalytic processes.

In recent years, nuclear magnetic resonance (NMR) has emerged as a powerful, often unique, technique for the study of solid materials, and the area of heterogeneous catalysis is a natural beneficiary of this development. The evolution of modern high-resolution solid-state NMR results largely from novel theory and experiment, in particular through significant advances in resolution, sensitivity, and selectivity. Beyond the advantages of high magnetic fields and multidimensional spectroscopy, NMR in solids has been transformed by the advent of coherent averaging techniques, including multiple-pulse sequences, cross polarization, and sample spinning. Research in NMR spectroscopy continues to produce advances in resolution and sensitivity. Examples include the invention of variable-angle techniques to achieve high resolution and correlations, rotational echoes and multiple-pulse recoupling to measure interatomic distances, and the use of superconducting detectors and optical pumping to achieve high sensitivity. The recent combination of magnetic resonance with detection by scanning tunneling and atomic force microscopy provokes the contemplation of truly

localized, single atom NMR, an appropriate goal in our imminent age of nano-scale and molecular catalyst design.

The "interface" between catalysis and NMR is currently an area of much activity, and it is the aim of the present volume to describe this interface. Topics have been selected to illustrate the scope of applications of NMR to the study of catalysts and catalytic processes. The contents of this volume provide illustrations of the principles of solid-state NMR, with applications to materials of relevance to catalysis, including zeolites and other molecular sieves, oxides, dispersed silica and alumina, supported metal systems, layered materials including clays, zirconium phosphates, metal sulfides and graphite, and to in-situ processes including diffusion and chemical reactions. The contributors to this volume are leaders in the field who have provided, following a brief introduction by the editors, seven chapters which we believe will form a useful resource for scientists and students interested in the principles and applications of NMR in heterogeneous catalysis.

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Alexander Pines

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Introduction

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I. CATALYSIS

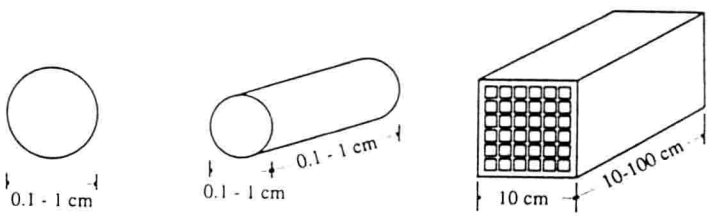
Many of the chemical reactions used to produce the materials, fuels, chemicals, and pharmaceuticals needed by modern societies could not be carried out in a practical fashion without the intervention of catalysts [1,2]. The first catalysts used by humans were the enzymes present in yeast. However, it was not until the nineteenth century that studies by Berzelius, Faraday, and others revealed that many inorganic substances could also serve as catalysts. Today, it is widely recognized that the range of substances serving as catalysts is quite broad, encompassing electrons, protons, hydroxyl groups, gases, organometallic complexes, metals, oxides, chalcogenides, and enzymes. The common property shared by all catalysts is the ability to interact with one or more reactants in such a way as to accelerate the transformation of these species into products without consumption of the catalyst in the process. In reactions where one or more products might be formed from a given set of reactants, selectivity for the formation of a single desired product is often achievable by the action of a suitable catalyst.

The success of the fuel and chemical industries as we know them is a direct result of the discovery of catalysts for carrying out specific reactions or sets of reactions at high rates and with high selectivity for the desired products. It is, therefore, not surprising that over 90% of the chemical processes in use require one or more catalysts. The preponderance of solid, or heterogeneous, catalysts

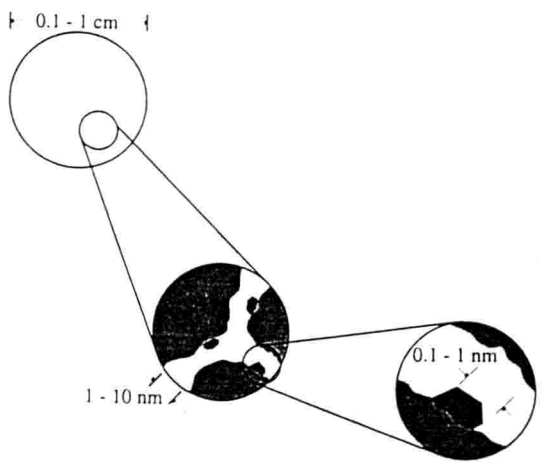
(including, for example, zeolites, oxides, sulfides, and metals) is a result of the ease with which such materials can be separated from products and unconverted reactants. Consequently, it is to *heterogeneous catalysis* that the chapters of this volume are devoted.

II. STRUCTURE AND PROPERTIES OF HETEROGENEOUS CATALYSTS

Most heterogeneous catalysts exist in the form of microporous solids. The catalysts are usually produced in the shape of spheres, cylinders, or monoliths, such as those shown in Figure 1. The internal surface area is typically 10–10^3 m^2/g. Catalysis occurs either on the surface of the microporous solid, as in the case of zeolites, or on the surface of microdomains of active material dispersed inside the microporous solid, as in supported metals, oxides, sulfides, etc. In either case, the high internal surface area of the microporous solid is used to obtain a high concentration per unit volume of catalytically active centers.



(A)



(B)

Figure 1

The reactants in a catalyzed reaction are present in either the gas or liquid phase, and in order to reach the catalytically active centers the reactants must diffuse through the pores of the catalyst, or catalyst support. Reactants in the immediate vicinity of the pore walls or the surface of the catalytically active components can interact with these surfaces by adsorption. This interaction ranges from weak (physisorption) to strong (chemisorption). Physisorption is governed primarily by dispersive forces and does not result in a chemical transformation of the adsorbate, whereas chemisorption is characterized by the formation of chemical bonds between the adsorbate and the adsorbent and can result in significant changes in the electronic properties of the adsorbate. The adsorbed reactants may undergo a variety of processes while on the surface of the catalyst. The simplest of these is surface diffusion in which the adsorbed material carries out a random walk on the catalyst surface. During diffusion, physisorbed material may become chemisorbed and vice versa. The adsorbed reactants may also leave the surface by desorption or, in the case of chemisorbed reactants, undergo chemical reaction. The reaction process can be unimolecular, as with the case of dissociation of a diatomic species, or bimolecular, as in the case of hydrogen abstraction or addition. The species formed via surface chemical reactions can serve as intermediates for other reactions, or they can desorb as final products. The products of catalyzed reactions can undergo all of the same processes experienced by reactants. Figure 2 illustrates two examples of such processes.

The observed activity of a catalyst is dictated by the intrinsic activity of the catalytically active component and by the effects of intraparticle mass transport.

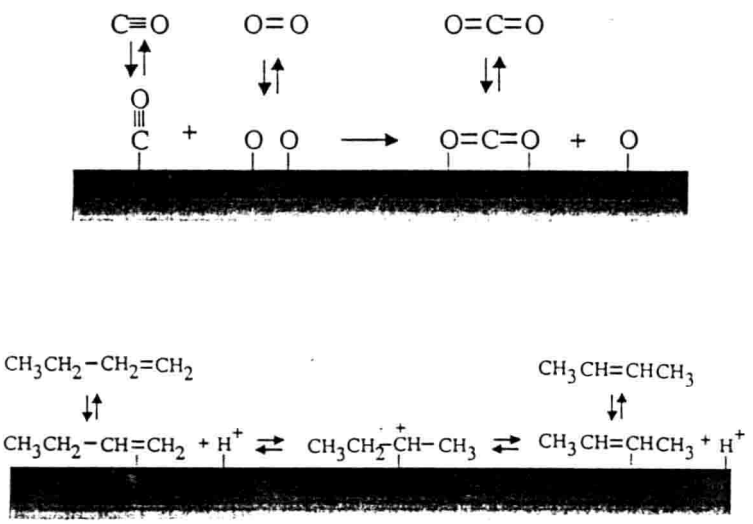


Figure 2