

Fundamental and Applied Catalysis

Catalytic Ammonia Synthesis

Fundamentals and Practice

Edited by J. R. Jennings

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Fundamentals and Practice

FUNDAMENTAL AND APPLIED CATALYSIS

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PRINCIPLES OF CATALYST DEVELOPMENT

James T. Richardson

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FOREWORD

The phenomenon of catalysis is found in many homogeneous and heterogeneous systems undergoing chemical change, where it effects the rates of approach to the equilibrium state in processes as diverse as those found in the stars, the earth's mantle, living organisms, and the various chemistries utilized by industry. The economies and the living standards of both developed and developing countries depend to varying degrees upon the efficacy of their chemical industries. Consequently, this century has seen a wide exploration and expansion of catalytic chemistry together with an intensive investigation of specific, essential processes like those contributing to life-supporting agricultures. Prime among the latter must surely be the "fixation" of atmospheric nitrogen by catalytic hydrogenation to anhydrous ammonia, still the preferred synthetic precursor of the nitrogenous components of fertilizers. In each decade contemporary concepts and techniques have been used to further the understanding, as yet incomplete, of the catalyst, the adsorbates, the surface reactions, and the technology of large-scale operation. The contributors to the present volume review the state of the art, the science, and the technology; they reveal existing lacunae, and suggest ways forward.

Around the turn of the century, Sabatier's school was extending the descriptive catalytic chemistry of hydrogenation by metals to include almost all types of multiple bond. The triple bond of dinitrogen, which continued to be more resistant than the somewhat similar bonds in carbon monoxide and ethyne, defied their efforts. During the following decade, Haber and Bosch developed their process for the large-scale production of ammonia by the hydrogenolysis of atmospheric nitrogen over promoted and stabilized, iron-based contacts: it was an epoch-making advance. The work assured not only adequate world food-production, but also gave impetus to the science of catalysis by solids and the associated chemical engineering. Exploding populations could now be properly provisioned with victuals or otherwise provided with munitions, while most of the essential empirical features of catalyst activity were revealed.

Professor Tamaru, prominent among catalytic chemists even as a babe-in-arms (photo page 5), tells something of the formidable minds and institutions which drove the research forward in a style now classic and probably unparalleled outside the German chemical industry. This paradigm of major invention possessed a

clearly defined objective, presented by an emergent universal need and a massive potential market. The objective was judged to be attainable by knowledgeable scientists despite uncertain data, and had champions among the most able contemporary industrial managers. The cognate sciences and technologies were pushed ahead by cooperating chemists and engineers, notably by men of broad and deep understanding. The science of both Haber and Bosch had an industrial background, making their story timely reading now that the so-called "relevance" issue intrudes increasingly upon the research within academic institutions, and as the higher management of industry becomes ever more remote from its scientific bases.

The magnitude of the achievements in the more quantitative, physical science of the Haber-Bosch program has tended to outshine the contributions from both the associated exploratory catalytic chemistry and the concepts derived therefrom. The work of Mittasch was absolutely vital and led ultimately to the development of the more effective catalysts which had commercial potential and to improved gas purification. As pointed out in this volume, some of those ideas have had to be abandoned, but it is inescapable that the notion of multifunctionality, implying jumpover, spillover, or switchover of intermediates, was contained therein, albeit formalized much later by Weiss and others. Indeed, phenomena at interfaces between solids remained unapproachable until the application of the latest physical techniques (Chapters 2-5).

The best testimony to the pioneers' accomplishments, beyond the award of two Nobel prizes, must be the fact that, after almost eighty years of research and development, the modern iron-based catalysts are hardly more than tidied-up versions of the originals. Subsequent improvements to the process have derived in the main from the generation of purer synthesis gases, the optimization of the preparation of the catalysts and their induction procedures, the determination of better kinetics (Chapter 6) with the consequent advance in the chemical engineering applications (Chapters 6 and 7). All of these improvements were directed to the lowering of reaction pressures and temperatures, and ultimately of capital costs.

To place the recent contributions on ammonia synthesis in context, the broad historical background on the one hand, and the sheer complexity of the operating process on the other must be considered. Prior to the advent of modern surface physics there existed a modest consensus among practitioners; the views were common but not universal, reasonable but equivocal, and often implicit rather than explicit. By the late fifties it had been accepted that the essential active phase is body-centered cubic metallic iron, that the likely most active crystal face is (111), that the refractory oxide components serve primarily to hinder sintering, and that one function of the alkali promoter is to lower, somehow, the work function of the iron. Already some believed that alkali metal, formed *in situ* by reduction under pressure as dilute adsorbed atoms, facilitated the transfer of electrons from the Fermi level of iron to the antibonding π -orbitals of physisorbed dinitrogen, and that a chemisorbed, "side-on" state of dinitrogen was possible (by analogy with contemporary hypotheses involving adsorbed ethene and ethyne as π -complexes on metals such as palladium). The anionic dinitrogen intermediate was not, however, perceived to be an adsorbate of measurable lifetime, although the existence of precursor states had just been signalled.

The second feature to be noted is the complicacy of the working industrial catalyst as compared with its models, which have often been devised as alkali metal-atom doped specific faces, planar or stepped, of massive single crystals of the purest iron, prepared with all the resources of high-vacuum technology. In contrast, real catalysts are porous aggregates of small particles, more or less crystalline, usually containing, beside iron and potassium, two or more refractory oxides of different acid-base properties. They are always prepared by hydrogen reduction of a somewhat inhomogeneous but intimate mixture of binary and ternary oxides of sufficient purity, thus inducing contingent, interdependent solid-gas and solid-solid, nucleated reactions, necessarily under finite partial pressures of water having catalytic or anticatalytic effects (Chapters 2, 3, 5, and 9). An adequate reproducibility of designed activity and life can be obtained only by rigid adherence to a set of procedures, scientifically based but established empirically; it usually involves some minor, intrinsic variability due to the exigencies of process control and the intrusion of hidden variables (e.g., dissimilar motivations among process operators and catalyst designers!). Oldsters would say that activity depends upon the "prehistory" of the catalyst; alteration of a component or a parameter entails a change of activity having downstream consequences in kinetics, incongruent reactor design, and costs, for which no algorithm yet exists.

Schlögl's article shows why. He tells of the application of old and new techniques to the characterization of the processes, phases, and interfaces occurring in the evolution of the working catalyst from its oxide precursors. He arrives at conclusions which are quite similar to those derived from chemical principles, while finding further complexities. It is in this area that surface physics demonstrates its greatest value to applied catalysts.

The electropositive-electronegative (basic-acidic, etc.) counterpoint runs through all catalysis, so that the various correlates of the promotor's polarity are no doubt to be detected at all stages of the genesis and maintenance of the active interface, and of its accessibility.

The desired holistic solution remains remote but is foreshadowed in the reports by Ertl, Somorjai, and Strongin on the interactions at the atomic level between adsorptives, surface geometries, promotors, and stabilizers in model catalysts. Ertl demonstrates the central role of a precursor state [the inclined α -state, $\text{metal}^+ - \text{N}_2^-$, on Fe(111), not unlike the "side-on" adsorbate suggested earlier] in the dissociative chemisorption, and its additional stabilization by potassium adatoms. He, and in a subsequent chapter Geus and Waugh, use the data to derive potential energy diagrams for the reaction chain, and from which they calculate overall reaction rates. Although there are some differences of opinion between the two groups, the fact that such methods give results of the right magnitude affirms the advance of the last decade.

Somorjai and Strongin extend the theme, narrowing the gap between the models and the real catalyst, especially to discern mutual effects in the Fe-Al-K-O-N-H system. As in the work described by Schlögl, some expected chemistry is found but it is illuminated by the discovery of unpredicted surface reconstructions in the presence of alumina and water. The presence of potassium adatoms, as such *in situ*, is discounted in favor of a KO_x adsorbate which retains the alkali while

yet stabilizing Ertl's precursor and also loosening the bound ammonia. In normal practice alkali compounds are not found downstream of industrial reactors, and one is reminded of the old observations on the photoelectric emission of complex surfaces which showed that alkali adatoms adjacent to oxygen adatoms (W-Cs-O) are not only more strongly bound but induce dramatic decreases in the work function. A clear definition of the role(s) of the alkali promotor, electronic, geometric, or both seems near, and although rather late in the history of ammonia synthesis must remain a major objective in view of the ubiquity of such effects in catalysis (Fischer-Tropsch, higher alcohols, etc.).

Impure feedstocks add other dimensions to the matrix; reactive contaminants usually behave as permanent or temporary poisons according to whether they are strongly or weakly bound to active sites under reaction conditions. Nielsen (Chapter 8) describes the principal types, e.g., inhibitors yielding strongly electronegative adsorbates (halogens, oxygenated, and sulfuretted species) or the rarer polyvalent adatoms (phosphorus, arsenic). He mentions the empirically determined tolerable concentrations and gives some quantitative analysis of the relationship with active area. The effects of chlorine on the alkali promotor provide a nice illustration of the acid-base counterpoint, and the acceleration of sintering by steam is an important example of a less well-known effect of steam, additional to poisoning. Some corresponding chemisorptions and solid reactions are included by Geus and Waugh (Chapter 5).

Nowhere is the reacting catalyst system at true equilibrium. Furthermore, much academic experimentation is done far from equilibrium, but the industrial reactor is designed to approach that state at its exit. In Chapter 6, Gramatica and Pernicone show how useful, essentially empirical, kinetic equations have been put together on the basis of the earlier classical adsorption isotherms associated with the names of Langmuir, Tempkin, and others. Kinetics which describe accurately the degree of advancement of the reaction with time, over a range of pressures, temperatures, and contents of common impurities, are vital to reactor and process design, and the authors give an outline of the procedures which have led to the evolution of the modern plant systems of Hooper's Chapter 7. It will be appreciated that the cost of the research and development leading to such kinetic equations, and their importance to competitive design, makes them a valuable commercial property.

However, the large investments in established processes and plants naturally impose an enormous inertia, among producers and contractors alike, toward all radical change. It is therefore exciting to escape from the claustrophobia of the iron-based Haber-Bosch system into the wider regions of the Periodic Table, and the "greener," more exploratory areas of homogeneous and enzyme catalysis, in the reviews by Tennison (Chapter 9) and by Leigh (Chapter 10). Anhydrous ammonia will continue to be the commodity in demand for the foreseeable future; dilute ammonia, commonly aqueous, incurs large cost penalties for transport and concentration unless made to suit local circumstances. So the first approach to novelty is by way of a radically new catalyst tailored to fit the existing type of plant, while any enzyme-like reaction must involve hydrogenated dinitrogen only as an intermediate en route to more complex compounds.

Tennison explores the patterns of behavior, in absorption, adsorption, and activity, among the transitional elements of the long periods, with timely emphasis upon the more precious metals and the alloys of iron with its base-metal congeners of group 8. The relatively high activity of the Fe-Ru-Os triad has long been known and, in the early days of the rigid-band theory of metals, was correlated with the presence of three "holes" in their *d*-bands. Japanese research in the last twenty years has restressed the possible potential of ruthenium as an alternative to iron and it is of great interest to see that its exploitation has become a distinct possibility. Currently, the preferred support appears to be carbon, a material whose properties can be so irreproducible that its use was once generally avoided, unless essential as in dispersing precious metals in hydrogenation catalysts for the fine-chemical and pharmaceutical industries. Alkali promoters are again necessary, and their function in the new catalysts is investigated in detail but with conclusions similar to those reached by the other authors. The ubiquity of the effect would seem to support a general electronic influence rather than sets of related geometries.

It is a cause for wonder that the elements iron and molybdenum should be so prominent in catalysts as diverse as the metalloenzymes of nitrogen-fixing bacteria and the Haber-Bosch contacts. Perhaps the link may lie in some similarity between the proposed active K-Fe-O surface complex and the organo-Fe(Mo)-S organo-Fe(Mo)-S complexes wherein the sulfur ligands maintain the metals in low valency states. Leigh surveys succinctly the enzyme field and the related models among the dinitrogen-carrying complexes which have raised many false hopes since the middle sixties and the isolation of the first such molecules; photo- and electrochemical inputs have been used but commercial applications are not yet feasible.

The implications of Leigh's view of future developments in nitrogen fixation apply equally to all catalysis: we are unlikely to find more targets as "simple" and profitable as ammonia synthesis. Even before interdisciplinary projects such as the forementioned photoheterogeneous catalysis, the coming years should see the coupling of heterogeneous with homogeneous catalysis as in the present pursuit of routes from methane to higher hydrocarbons using radicals generated at oxide surfaces. It is known already, for instance, that oxygen can be hydrogenated to yield aqueous hydrogen peroxide, which with Fenton's reagent forms hydroxyl radicals and thence phenol from benzene continuously. Similarly, nitric oxide gives hydroxylamine and amidogen radicals. The core of the problem is to target a valuable product other than ammonia (an amino acid or a nitrogen heterocycle, say) and then to devise means for its economic extraction. The field is not at the present time sufficiently developed to allow this to be done, in either its chemistry or its chemical engineering.

D. A. Dowden

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PREFACE TO THE SERIES

Catalysis is important academically and industrially. It plays an essential role in the manufacture of a wide range of products, from gasoline and plastics to fertilizers and herbicides, which would otherwise be unobtainable or prohibitively expensive. There are few chemical- or oil-based material items in modern society that do not depend in some way on a catalytic stage in their manufacture. Apart from manufacturing processes catalysis is finding other important and ever increasing uses; for example, successful applications of catalysis in the control of pollution and its use in environmental control are certain to increase in the future.

The commercial importance of catalysis and the diverse intellectual challenges of catalytic phenomena have stimulated study by a broad spectrum of scientists, including chemists, physicists, chemical engineers, and materials scientists. Increasing research activity over the years has brought deeper levels of understanding, and these have been associated with a continually growing amount of published material. As recently as sixty years ago, Rideal and Taylor could still treat the subject comprehensively in a single volume, but by the 1950s Emmett required six volumes, and now no conventional multivolume text can cover the whole of catalysis in any depth. In view of this situation, we felt there was a need for a collection of monographs, each one of which would deal at an advanced level with a selected topic so as to build a catalysis reference library. This is the aim of the present series, Fundamental and Applied Catalysis.

These books in the series will deal with particular techniques used in the study of catalysts and catalysis; these will cover *the scientific basis of the technique, details of its practical applications, and examples of its usefulness*. The volumes concerned with an industrial process or a class of catalysts will provide information on the *fundamental science of the topic, the use of the process or catalysts, and engineering aspects*. For example, the inaugural volume, *Principles of Catalyst Development*, looks at the science behind the manufacture of heterogeneous catalysts and provides practical information on their characterization and their industrial uses. Similarly, an upcoming volume on ammonia synthesis will extend from the surface science of single iron crystals to the design of reactors for the special duty of ammonia manufacture. It is hoped that this approach will give a series of books that will be of value to both academic and industrial workers.

The series will deal with both heterogeneous and homogeneous catalysis, and will include processes in the heavy chemicals and oil refining industries, the smaller-scale manufacture of pharmaceuticals, and various aspects of pollution control. The series editors would welcome any comments on the series and suggestions of topics for future volumes.

Martyn Twigg
Michael Spencer

Billingham and Cardiff

PREFACE

The story of the catalytic synthesis of ammonia from its elements ranks as a classic in the development of the chemical industry during the twentieth century. The enabling research work began at a time when it was not even known whether the required reaction between hydrogen and nitrogen was thermodynamically feasible. Nevertheless, several leads from different research groups were followed and this culminated eventually in the demonstration by Fritz Haber of the catalytic synthesis of ammonia at elevated pressures. The major new technologies of catalyst promotion and high-pressure chemical engineering were born and new challenges associated with stress corrosion were presented to the metallurgists. That these problems were solved is now history, due to the efforts of Alwyn Mittasch, Carl Bosch, and many others. The lead in high-pressure technology gained by BASF also resulted in the development of the first process for the production of synthetic methanol by the hydrogenation of carbon monoxide. So successful were the team from BASF in their development of the ammonia synthesis reaction that, after the initial breakthrough, most of the subsequent major developments have been in the generation and purification of synthesis gas.

Scientific studies on the precursor and the active catalyst followed rapidly and the adsorption studies of Emmett and his colleagues set the principles which are still used in the development and understanding of most new catalysts, even today. A high level of understanding of the catalyst was gained in the early studies, but it was the development of ultrahigh vacuum (UHV) techniques and electron spectroscopy which led to the advances in the seventies and eighties. Fascinating differences in the reactivity and properties of iron crystals, according to which the crystallographic plane was examined, have emerged. Furthermore, some correlation between UHV data and kinetic measurements under process conditions can now be made.

Amid the excitement of this "UHV era" substantial progress was being made on the process itself. Operating pressures and temperatures have gradually been reduced in the quest for maximum efficiency in the use of energy, and new low-pressure processes are available in the market for license. The possibility remains that with further catalyst development, including perhaps the use of precious metal catalysts, the severity of the process conditions may be reduced further still.

All of the authors who have contributed to this volume are true experts in their chosen field of study and have a wealth of experience in the science and technology of ammonia synthesis. Both academia and industry are well represented and this leads to a fine balance between the science and the technology. Furthermore, in keeping with the international nature of the ammonia business, the range of authors also represents a wide geographical spread. The book begins with a history of the early developments of ammonia synthesis leading to four chapters devoted essentially to fundamental scientific investigations of the catalyst and its promoters. Three chapters on technological aspects of ammonia synthesis follow: kinetics, commercial operation, and catalyst deactivation. The book then concludes with chapters on novel alternatives to the conventional promoted iron catalyst and some thoughts as to how the ammonia synthesis industry might develop in future years.

We have endeavored to present a complete but balanced view of ammonia synthesis at a time when both the science and process are relatively mature. It is, however, a sobering thought that despite all the high-quality studies on this simplest of reactions, some questions still remain to occupy the minds of scientists in the years ahead.

All of the people concerned with this book were saddened by the death of Giorgio Gramatica while the volume was in press, and we regret he was unable to see his chapter, coauthored with Nicola Pernicone, in its final published form.

J. R. Jennings

Middlesborough

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