EXPERIMENTAL METHODS IN CATALYTIC RESEARCH

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PREFACE

In this century catalysis has advanced from a laboratory curiosity to a major component of the chemical and petroleum industries. The development of catalysts was initially a mysterious art requiring laborious empirical testing. Testing of this type will probably always be a part of catalyst development, but the process can be performed expeditiously by utilizing the vast store of scientific and practical information currently available and by employing modern research tools. Concurrent with the development of practical catalysis, new research tools were applied to the investigation of catalysts and catalytic reactions. Some of these new experimental procedures were developed especially for the study of catalysis and others were adapted from the areas of chemistry and physics. The improved research tools and the new theoretical concepts resulting from their use have dispelled many of the mysterious aspects of catalysis; however, they have disclosed a host of new and challenging problems. Since 1935 the experimental methods used in catalytic research have increased both in number and complexity, so that mastery of all of the techniques available is difficult. The present treatise provides in a single volume a useful account of procedures written by specialists in different areas of catalytic research. Each chapter includes a description of the method and its fundamental principles, the apparatus used, the data obtained and their interpretation, and, finally, an account of special problems related to catalytic research.

The authors were asked to describe their speciality at a level understandable to a physical chemist with no experience in this field. Their accounts were to provide an adequate introduction to both the experimental procedures and the theory. To a large degree these objectives have been accomplished.

The book is divided into four parts. The first part, Chapter 1, describes methods for determining the kinetics of catalytic reactions (including experimental reactors in which the complications of mass and heat transfer are avoided or minimized), the use of tagged molecules, and poisoning. The second part, Chapter 2, presents methods for elucidating the physical structure of catalysts, their surface areas, and pore geometry. The third section, Chapters 3 to 9, describes methods for determining chemical and physical characteristics of surfaces and the nature of adsorbed species, including contact potentials, spectra of adsorbed molecules, and acidity of surfaces. This part also presents the specialized techniques for electron and field-ion emission microscopy, low-energy electron diffraction, ultrahigh vacuum investigations, and the determination of electrical properties of catalytic materials. The fourth section, Chapters 10 and 11, describes the measurement and interpretation of magnetic properties of catalysts by conventional techniques and electron spin resonance.

For a subject as broad as modern catalytic research, the inclusion of all pertinent topics is beyond the scope of a single volume. The preparation of catalysts was not included as this topic seemed adequately described in the last decade in Emmett's "Catalysis"; however, the preparation of crystalline aluminosilicates has emerged as a new procedure. Conventional electron microscopy and x-ray and electron diffraction were omitted because these methods have not changed significantly in recent years. A number of research tools that were not included for diverse reasons include the electron-probe microanalyzer, and apparatus for studying electrode reactions, x-ray absorption edge phenomena, and the Mossbauer effect.

Finally, the editor acknowledges the outstanding contributions of Professor Paul H. Emmett to heterogeneous catalysis, especially in the development and use of new research tools. For more than thirty years Paul Emmett has been the kindly adviser of many young and not so young catalytic chemists.

Hamilton, Ontario, Canada
March, 1968

R. B. ANDERSON

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KINETICS OF CATALYTIC REACTIONS

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I. Introduction

Catalysis is a kinetic process. A large fraction of catalytic research involves investigation of kinetic phenomena, i.e., quantitative studies of reaction rate and factors influencing rate. The catalyst increases the rate and/or directs the reaction to form desirable products. The final criterion of the value of any catalyst is its behavior in the chemical reaction of interest; therefore, kinetic experiments are important and should be designed sensibly. The ultimate goal of kinetics is to develop a fundamental rate equation that fits the kinetic data and is consistent with observations on the reaction mechanism. Burwell (*23*) defined the mechanism of a catalytic reaction as "the residuum left after the elimination of the other conceivable mechanisms by any kind of information." The same criterion may be applied to fundamental rate equations. However, the attainment of more limited objectives, such as a useful empirical rate equation, is valuable in understanding and using the catalytic process. Generally, kinetic measurements alone do not provide a complete description of the catalytic reaction since the kinetics are concerned primarily with the slower steps of the reaction sequence.

Rate studies of catalytic reactions are made in a variety of ways for purposes varying from empirical activity tests to engineering investigations to fundamental kinetic studies. This chapter is concerned with methods for obtaining reliable kinetic data in laboratory or benchscale reactors.

Generally, the task of finding kinetic equations for the reactions at the catalyst surface is sufficiently difficult that complications by mass and heat transfer should be avoided to the extent possible. Solutions of differential equations for reactions coupled with mass and heat transfer can be obtained by numerical methods for model systems of moderate complexity, and a substantial literature is available for which the following references provide an introduction (*65*, *67*, *79*, *81*). Usually, simplifying assumptions are made concerning particle shape and the nature of the pore structure, and a solution is obtained for a given rate equation. Exact solutions of the differential equations, if possible, often have little advantage over numerical solutions, because the exact solution is usually too complicated to permit simple plotting of experimental data. The investigator must resort to matching curves often having few distinctive characteristics. The conclusion to be drawn from this discussion is that the investigator should avoid if possible the complexities of mass and heat transfer in determining the kinetics of a catalytic reaction. Once the kinetics are established, the results can be extrapolated to the practical situation in which mass and heat transfer are important to a reasonable degree of approximation. Practical guide lines for estimating the importance of heat and mass transfer in catalyst beds have been given (*82*). The object of the investigation should be to determine the kinetics of the reaction at the surface without other complicating factors.

Useful reactors have simple flow patterns in which either mixing does not occur or is complete. Ideally, the catalyst bed should be isothermal, interand intraparticle mass and heat transfer should be rapid compared with reaction rate and heat generation, and the flow pattern should be either of the piston type or of the thoroughly stirred type. Other requirements for simple kinetic experiments are constant catalytic behavior over substantial periods of time, preferably days, and accurate analytical methods for some or all of the components of the reactants and products.

By choice of the proper reactor or by diluting the catalyst with inert particles, intraparticle mass and heat transfer can usually be eliminated as important factors. Interparticle mass and heat transfer, however, are catalyst properties, but the effect of these transport processes can be minimized by decreasing the particle size. These problems can sometimes be avoided by determining the kinetics under conditions in which the reaction is slow or by preparing special catalyst particles by coating inert spheres or cylinders with a thin layer of "the active catalyst" (*24*). We note, however, that in the first method the kinetics and mechanism of the reaction may change if, for example, temperature or pressure is decreased substantially, and in the second case, the special catalyst may not be typical of a given practical catalyst even if the preparation is similar.

In practice the worker should first make activity tests of catalyst samples of different particle size. If the activity per unit weight of catalyst increases with decreasing particle size and eventually becomes constant, the particle sizes for which the activity is constant are probably not limited by intraparticle mass transfer. Intraparticle mass and heat transfer limitations will change the temperature dependence of constants of the rate equation. For mass transfer limitations the apparent activation energies should decrease with increasing temperature, and for heat transfer the apparent activation energies should increase with increasing temperature for exothermic reactions and decrease for endothermic reactions. Gross overheating in fixed beds may be detected by direct temperature measurements, except in beds highly diluted with inert solids, or by observing changes in conversion over a range of temperature. If on increasing temperature the conversion increases abruptly from a low to a high value, and if the converse occurs on decreasing temperature, the catalyst bed is overheating substantially.

Only fixed beds and stirred reactors are considered in this chapter, since only these types (when properly used) yield data that can be interpreted directly. Small fluidized-bed reactors are unsuitable for basic kinetic studies, because the patterns of gas flow and catalyst mixing are not simple, and, possibly of equal importance, proper fluidization occurs only within a very limited range of gas flow.

The author has assumed that the reader has some knowledge of reactors and components of experimental systems. In most instances general rather than detailed descriptions of reaction systems are given, because each combination of reaction and catalyst may require special features. The experimenter will usually profit by designing a reaction system appropriate to his problem rather than adapting apparatus used in other work. At the present time excellent devices for measurement and control are available commercially as well as reliable valves and fittings for systems operating at moderate-to-high pressures; therefore, these components are not considered. Throughout the chapter, only systems employing solid catalysts are described; however, the section on stirred static reactors is applicable to homogeneous or immiscible-liquid catalysts.

Definitions of differential reaction rate and selectivity are given first, followed by a description of flow- and static-type reactors and the methods of interpreting rate data. The third section considers some experimental details concerning small reactor systems such as reactors and heating media. The final part of the chapter presents some selected topics on catalytic kinetics including pretreatment of catalysts, preparation of evaporated metal films, empirical analysis of data, and, finally, a moderately long account of poisoning experiments.

II. Definition of Reaction Rate and Selectivity

For any type of reactor certain component(s) of reactants or products must be chosen as indicative of the forward progress of the reaction. For reactions with simple stoichiometry, such as the ammonia synthesis, any component of reactants or products can be chosen to calculate the reaction rate. However, the fraction of ammonia in the exit gas can be determined accurately and rapidly, and the differential reaction rate is usually based on this quantity. For more complex catalytic processes with variable stoichiometry the choice of components becomes somewhat arbitrary, but the selection must still be based on the availability of simple analytical methods of moderate-to-high accuracy. The Fischer-Tropsch synthesis on iron or cobalt appears to proceed according to the following consecutive reactions*:

$$2H_2 + 1CO \rightarrow (1/n)(CH_2)_n + H_2O \tag{1}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{2}$$

---

* The actual situation is somewhat more complex since paraffins and oxygenated molecules are also produced.

Here the hydrocarbon distribution varies from methane to high molecular weight waxes, and a complete analysis of the hydrocarbons is not possible on small samples from laboratory reactors. The rates can be based on components of the feed, H_2, CO, or $H_2 + CO$; the latter choice has advantages since 3 moles of $H_2 + CO$ yields 1/n moles of $(CH_2)_n$, irrespective of the ratio of H_2 to CO consumed, and this relationship also holds for reactions of the following types that normally do not occur in the Fischer-Tropsch synthesis:

$$3H_2 + CO_2 \rightarrow (1/n)\,(CH_2)_n + 2H_2O \tag{3}$$

and

$$H_2O + 3CO \rightarrow (1/n)\,(CH_2)_n + 2CO_2 \tag{4}$$

This definition of rate is not influenced by the water–gas shift [Eq. (2)] since 1 mole of CO yields 1 mole of H_2.

For a stirred reactor the differential reaction rate r is expressed as

$$r = (1/W)\,dn_i/dt \tag{5}$$

where n_i is the number of molecules of reactant(s) or product(s) i consumed or produced, t is time, and W is some measure of the amount of catalyst present, weight, volume, weight of active component, or surface area. For fixed beds of catalyst in which the rate is a function of bed position, Eq. (5) must be applied to differential increments of the bed, as will be described in the next section.

In flow reactors, formulation of the differential reaction rate in terms of contact time has led to incorrect equations, even by experts. The flow balance method of Hougen and Watson (*44*) is preferable since the correct equation is obtained directly.

For reactions in which two or more products are possible thermodynamically, such as the Fischer-Tropsch synthesis or hydrorefining, basing the rate on feed components is convenient and usually proper. The formation of products may be expressed in terms of quantities called "selectivities." The tendency of a catalyst to produce a particular product or product fraction has been expressed in many ways in the literature; however, some definitions are difficult to justify. The selectivity J_h for production of component h, may be defined as

$$J_h = \Delta M_h/\Delta M_i = m_h/x_i \tag{6}$$

where ΔM_h is the quantity of h produced when ΔM_i of reactant i is consumed, m_h is production of h per unit amount of i introduced into the reactor, and x_i is the fractional conversion of i. Consistent units should be used in Eq.

(6), such as moles per mole or weight per weight, and reactant(s) i should be the same as those defining the reaction rate. Occasionally mixed units are used, particularly when some products of interest are distillation fractions; e.g., in the Fischer-Tropsch synthesis selectivity is often expressed as grams of product per standard cubic meter of $H_2 + CO$ consumed.

The selectivity J_h is an integral quantity expressing the production of h from zero to time t in a static reactor or from the inlet to a certain position in the bed for a flowing system. (For simplicity in discussing flow reactors, consideration is given only to a system with a constant feed rate where time is varied by changing bed length.) Differential selectivities j_h expressing the instantaneous production of h at time t or a given position in the bed may be expressed as

$$j_h = dM_h/dM_i = dm_n/dx_i \tag{7}$$

The product of rj_h is the instantaneous rate of production of h at a given time or position in the bed. At least in principle the differential selectivity may be related to temperature and the partial pressures or concentrations of reactants and products at a given time or bed position. Selectivity equations plus the rate equation for the overall reaction provide a complete mathematical description of the rate of formation of products. Unfortunately, the overall accuracy of most experimental measurements is often too low to permit differentiation of selectivity data, and differential selectivities have been considered in only a few instances, e.g., for the relative usage of hydrogen and carbon monoxide in the Fischer-Tropsch synthesis (*5*).

III. Types of Small Experimental Reactors

In this section reactors are considered according to the following outline:

A. Flow Reactors
  1. Integral Fixed-Bed Reactors
  2. Differential Reactors
  3. Stirred Flow Reactors
  4. Microcatalytic Reactor of Pulse Type
B. Static Reactors

In the schematic drawings depicting reactors, Figs. 1 and 2 and 4–6, sectioned and crossed-hatched areas have the following significance:

▧ Heating media and/or insulation
▨ Fixed bed of inert solids for preheating
▩ Fixed bed of catalyst

Flow reactors are frequently used in studies of catalytic kinetics and will be discussed first.

A. Flow Reactors

1. *Integral Fixed-Bed Reactors*

Here the reactor is usually a cylindrical tube of an inside diameter of 1.5 cm or less with a device for retaining the catalyst within a definite zone and surrounded by a medium of constant temperature as shown in Fig. 1A. The feed enters at a measured constant flow, passes through a preheater section, and through the catalyst bed to a section for recovering or measuring products. Appropriate compressors, feed pumps, reducing valves, and back pressure regulators must be employed to maintain constant operating pressure. For gaseous reactants, gas cylinders are a convenient source of pressurized gas. Small liquid feed pumps are discussed subsequently.

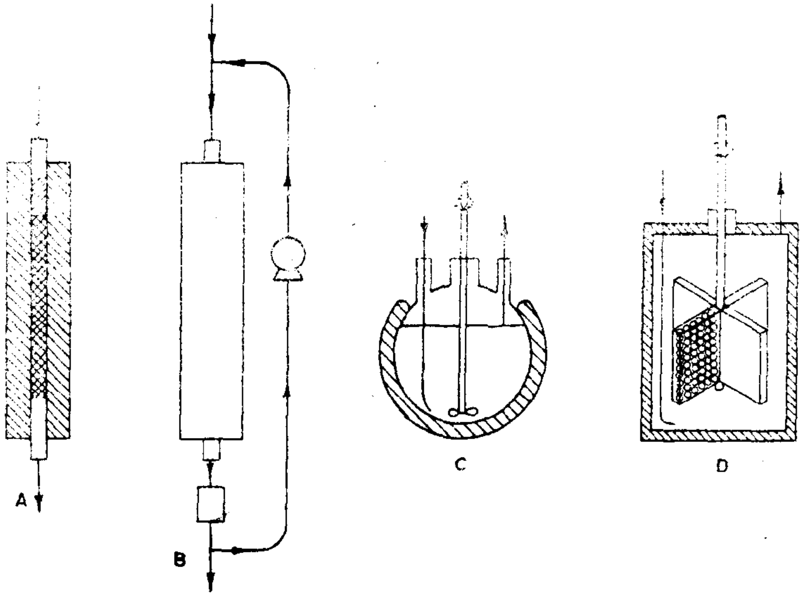

Fig. 1. Schematic of flow reactors: (A) single-pass fixed-bed reactor; (B) fixed-bed reactor with recycle. Reactor details are the same as in (A); (C) simple stirred reactor for use with liquids and powdered catalysts; (D) Carberry fixed-bed stirred reactor. Vanes are baskets of metal screen. Catalyst is shown in only one vane.

For the integral reactor the differential reaction rate may be defined by the equations of Hougen and Watson (*44*) for piston-type flow. To insure