ADVANCES IN CATALYSIS

VOL. XIII

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME 13

EDITED BY

D. D. Eley *Nottingham, England*	**P. W. Selwood** *Evanston, Illinois*	**Paul B. Weisz** *Paulsboro, New Jersey*

1962

ACADEMIC PRESS, NEW YORK AND LONDON

Contributors

R. COEKELBERGS, *Ecole Royale Militaire, Institut Interuniversitaire des Sciences Nucléaires, Brussels, Belgium*

A. CRUCQ, *Ecole Royale Militaire, Institut Interuniversitaire des Sciences Nucléaires, Brussels, Belgium*

A. FARKAS, *Houdry Process and Chemical Company, Marcus Hook, Pennsylvania*

A. FRENNET, *Ecole Royale Militaire, Institut Interuniversitaire des Sciences Nucléaires, Brussels, Belgium*

L. H. GERMER, *Bell Telephone Laboratories, Murray Hill, New Jersey*

G. A. MILLS, *Houdry Process and Chemical Company, Marcus Hook, Pennsylvania*

CHARLES D. PRATER, *Socony Mobil Oil Company, Incorporated, Research Department, Paulsboro, New Jersey*

F. S. STONE, *Department of Physical and Inorganic Chemistry, University of Bristol, Bristol, England*

JAMES WEI, *Socony Mobil Oil Company, Incorporated, Research Department, Paulsboro, New Jersey*

PAUL B. WEISZ, *Socony Mobil Oil Company, Incorporated, Research Department, Paulsboro, New Jersey*

Quo Vadis Catalysis

A Preface

Some years back one of our colleagues, leaning back in his chair with a gaze towards the future, was heard dreamily to utter the words: "Some day we shall know *the* secret to catalysis." Somehow this moment has haunted our memories. We remember the brief moment of euphoria which seemed to overcome us at the thought of this beautiful prospect; and then the moments of reflection which agonizingly continued to suggest that as surely as this thought was beautiful, there was something erroneous buried in its beauty. Years later the words would still echo in our memory. We suppose the reason being that it reflected a question which many (including ourselves) may have loosely or seriously entertained. Was there going to be a last volume of the *Advances in Catalysis*, containing a single and final chapter on *the secret?*

Can we expect a simple answer to why a catalyst X should have the power of making A react with B?

In the whole of "chemistry" we have been dealing with the basic question of why two molecules A and B *are* reactive to a certain degree; or, why they are reactive at all. Why is A more reactive toward B than toward B′? What is the cause of this chemical specificity? In the very process of exploring these questions we have created an inorganic chemistry, an organic chemistry, a biochemistry, ionic reaction mechanisms, quantum chemistry, molecular orbital models, Ligand field theories, and the like. We seem to be content (or at least moderately so) to recognize that, although the unifying theory to all chemical reactivities is available to us, in principle, in the form of polyelectronic wave-mechanics, its complexity is too great to be manageable much beyond the simplicity of a hydrogen molecule. Hence; we silently accept the need for staking out certain limited areas within the myriad of various types of atomic arrangements (molecules), wherein certain not-so-general but manageable mechanistic models and theories aid us in our understanding and extrapolation of chemical experiences.

Should we seek to study the reason for reactivity of A to B *in the presence of X* with *more* intense demands for a simple unifying answer? Obviously, in this task, we take on all of chemistry above, except that each *n*-body problem (reactivity of A and B) in chemistry, now becomes at least an $(n+1)$-body problem in catalytic chemistry (A and B and X). This recognition should calm our ambitions a little.

But perhaps the "presence of X" involves a special phenomenon quite different from the problems of chemical reactivities among A, B, B′, etc.?

Indeed, the originally suggested concept of catalysis took on the apparent attire of strict chemical noninvolvement; the catalyst X was not "consumed" but merely "present."

It seems we have matured to the realization that any influential effects must imply *involvement* through *some* sort of force fields between catalyst and reaction partners; we acknowledge these forces to be electronic and therefore chemical in nature, and thus we imply the existence of at least temporary chemical complex or bond formation with the catalyst. Clearly then, the n-body problem of chemistry (e.g., of A and B) becomes at least an $(2n+1)$-body problem (A, B; X; AX, BX) of catalytic chemistry (even before we worry about such strictly additional problems as energy heterogeneity of sites, polyfunctional catalysis, side reactions, etc.).

This logical sequence of concepts suggests a simple definition of catalysis, namely: *A chemical rate process is catalyzed when it requires the formation of a steady state concentration of a chemical combination of at least one of the reaction partners with another chemical agent, as the catalyst.* For example, with X catalyzing the transformation $A + B \rightarrow AB$, we may have

$$\begin{aligned} A + X &\rightleftharpoons AX \\ B + AX &\rightleftharpoons AB + X \end{aligned}$$

or,

$$\begin{aligned} A + X &\rightleftharpoons AX \\ B + X &\rightleftharpoons BX \\ AX + BX &\rightleftharpoons ABX_2 \\ ABX_2 &\rightleftharpoons AB + X + X, \end{aligned}$$

or several other possible variations as regards detail, but not in principle. Having arrived at this definition by small steps of reasoning we find that we have been well anticipated by J. A. Christiansen in an earlier volume of these *Advances* in the course of a more rigorous analysis in "The Elucidation of Reaction Mechanisms by the Method of Intermediates in Quasi-Stationary Concentrations" (Vol. V, p. 311 ff.).

With the events reduced to a set of chemical reactions, what happens to the historical concept that catalyst must not be "used up"? Once the *steady state concentration* of complex or compound involving catalyst has been produced, (and which itself can be considered as reversibly recoverable *after* contact), there is no net consumption. Continuing catalyst consumption would take place if the catalyst complex is not *physically retained* in the reaction space, but this represents an incidental (and well known) "engineering" circumstance. The *heterogeneous* catalyst facilitates this purely "engineering" circumstance. We might add the observation that in the case of a solid catalyst it becomes inherently difficult to measure or even detect the initially produced steady-state quantity of "reacted" catalyst, as the surfaces alone (or only parts thereof) are involved in this "consumption."

As we cast the catalytic reaction into a sequence of fairly ordinary steps of chemical interaction kinetics, we return to contemplate our simple "secret": We conclude that there is *no fundamental* difference between attacking the problem of catalytic reactivity and *the entire scope* of chemical reactivity, but the former must involve relatively *greater complexity;* if we put side-by-side the boxes which each contain one of the various fields of endeavor concerning molecular processes (inorganic chemistry, organic chemistry, biochemistry, enzymology, quantum chemistry, etc., etc.), we find ourselves—as catalysis researchers—defining for ourselves not an additional vertical box but a certain horizontal slice through all of them. In some ways we claim to exercise a "unifying" action across them, for the definition of the catalytic process describes the relatively simple unifying principle which defines the slice we make across the "disciplines" or "sub-disciplines" of molecular interactions. Perhaps *this* principle is the only simple secret, and beyond this we cannot hope to get simpler than the whole of chemistry.

So we do not feel too bad that the final chapter is not at hand; and that on the contrary, we are—in this six-chapter volume of the *Advances in Catalysis*—penetrating deeply into the heart of quite a number of major portions of the broad realm of catalysis:

An intensive review (F. S. Stone) examines experimental work and interpretation of interactions where the reactants (A, B, etc.) are some of the simple gases, oxygen, hydrogen, carbon monoxide, and carbon dioxide, and the catalyst (X) is one of a few selected oxide solids. We are carried to vivid realization of the importance of electronic phenomena by the experiences of photon-influenced chemisorption and catalysis on these solids.

Another chapter (R. F. R. Coekelbergs, A. Crucq, and A. Frennet) carries us into the relatively new field of radiation catalysis, where A, B, . . . , and X are not a closed or thermal system, but receive discrete forms of energy; specifically where the solid catalyst acts as a transducer for passing the energy of high energy nuclear radiation to a gaseous chemical reaction system.

As we have noted, the set of reaction rates which interconnect various chemical species are the most important properties in any catalytic experience, or investigation; it is a pleasure therefore to devote a large section (J. Wei and C. D. Prater) to notable advances in the analysis and interpretation of measured transformation rates in terms of the actual individual reaction rate parameters between transforming species of a complex system (and any system with more than two interconverting materials is complex!). Although this work may appear to be highly mathematical to those who only glance at the print, it is, in fact, highly descriptive and physically most meaningful for direct use by the experimentalist. Its meaning and practical utility span the entire field of all rate process studies and kinetics from chemistry to enzymology.

Broad are the implications and application of the principles of polystep reactions on polyfunctional catalyst combinations (P. B. Weisz). Here we deal with reaction sequences in which *two* catalyst species X *and* Y (or more) participate in one set of reaction sequences. Some of the general principles combine thermodynamics and physical parameters to yield important information and criteria for such rate processes, generally whether they occur in hydrocarbon transformations, organic chemistry, in a petroleum plant or in a living cell.

We have seen much work done with such "pet" chemical systems as hydrogen-deuterium exchange, hydrocarbon conversion, or carbon monoxide oxidation, and have felt that new insights may well be gained from studies in depth of more varied chemical systems; the transformations of the $—N=C=O$ group (isocyanates) are an example of such a class (A. Farkas and G. A. Mills). They are involved in some large scale chemistry of present-day polymer technology. Theoretically, this molecular system begins to bring along many of the subtle effects of electronic and steric detail on reactivity which attain full magnitude in biochemical systems.

Inasmuch as catalytic chemistry involves very special chemical complexes, in small concentrations, and in special places like only the surface of a solid, the development of new techniques suitable for the development of new information is always of great importance to the field. The development of low energy electron diffraction by back-reflection from surfaces to a new and powerful research tool (L. H. Germer) marks a recent such advance reported in this volume. It presents another potentially important route to direct "inspection" of the structural detail of the surface of X or the complexes AX, on solids.

The image of the catalytic researcher is assuming an ever increasing variety of arms and legs as it becomes a superposition of very many individual images, which coincide strongly only in the common core of the "catalyzed" rate process—as described by perhaps a definition as we tried above. We expect to find some of the most exciting and rewarding developments resulting from an ever increasing amount of "coupling" between disciplines. It will be the continuing goal in this series to call upon relevant progress in many areas of investigative endeavor.

July, 1962 P. B. WEISZ

Professor W. E. Garner

It was a sad moment for his friends and colleagues in chemistry departments throughout the world, to read of the death of Professor Garner on March 4th, 1960. He was particularly well known to catalytic chemists, by his papers over some thirty years, and by his effective contributions to the series of conferences on catalysis which were initiated by the Faraday Society Discussion at Liverpool in 1950. Many readers of this notice will remember hearing his paper presented to the First International Conference on Catalysis at Philadelphia in 1956, and will recall with pleasure his characteristically modest, yet persuasive contributions in discussion. Garner's influence extended far beyond his own research group at Bristol, his leadership and inspiration being felt over a wide circle of scientists.

As befitted a student of Professor F. G. Donnan, Garner possessed wide interests, and was a connoisseur of painting, silver, and ceramics. A pleasant recollection is that of a visit in his company, and that of a colleague, to the Washington Art Gallery. Characteristically, Garner's comments were few in number, but possessed that illuminating quality expected from a true collector. A kindly man, and of equable temperament, Garner's judgment in chemical problems and University affairs was eagerly sought by his lecturers and students, as they successively secured professorships or distinction in industrial science and government. He was unsurpassed as a chairman of committees, where his natural sympathy for the viewpoints of his fellow members ensured easy cooperation.

Professor William Edward Garner was born in 1889 and studied chemistry at the University of Birmingham. In 1913 he was awarded an 1851 Exhibition Fellowship to work with Professor Tammann at Göttingen. Returning to England at the outbreak of the First World War, he worked at Woolwich Arsenal on problems concerning high explosives. He retained an interest in this subject for the whole of his life, publishing important papers, both on flames and gaseous explosions and on the decomposition of solid azides. In 1919, Garner returned to Birmingham University as an assistant lecturer, but soon left for University College, London, where he worked in Professor F. G. Donnan's department until 1927. Garner's work during this period covered a very wide field of activity and included an interest in the physical chemistry of biological systems. This interest saw fruition some twenty years later in the encouragement of similar studies in his department at Bristol and the commencement of a School of Biological Chemistry in that University. In

1927 he was appointed Leverhulme Professor of Physical and Inorganic Chemistry at the University of Bristol. In the period up to 1939 he was especially active in the fields of gaseous explosions, heterogeneous catalysis, and heats of adsorption, and the kinetics of solid decomposition reactions. His studies of nucleation in solids, which he related to the general theories of solid state physics, put this subject on a precise basis. His calorimetric studies of adsorption on metallic oxides are classical, and formed a springboard for his subsequent intensive development of this subject. During the 1939–1945 war, Garner's department was largely devoted to government explosives research, while he played a big role in this field. He was appointed Chief Superintendent of Armaments Research in 1944, and his war-time efforts were recognized when he was made a C.B.E. in 1946.

From 1945, until his retirement in 1954, Garner's research efforts were largely in the field of chemisorption and catalysis on metal oxides. The observations of Garner, Gray, and Stone on the effects of adsorbed gases on the semiconductivity of cuprous oxide, formed the growing point for a thorough study of certain oxide systems using the methods and concepts of solid state physics. He was particularly happy correlating the findings of these newer approaches with those of the classical calorimetric method. Garner also gave active encouragement to similar studies on metals, alloys, and enzymes. Garner took the lead in organizing many Faraday Society Discussions, the repercussions of which would resound in his department in the following weeks. As an example, shortly after the war, Garner became convinced that free radicals played a role in biological reactions, but the present author had regretfully to report that the para-ortho conversion of hydrogen was too insensitive to test this view. However, with the advent of electron spin resonance techniques this has become a fruitful field of research. Garner's great success as a laboratory director was due to his ability to stimulate both discussion and experiment on current problems of this type.

Garner was elected a Fellow of the Royal Society in 1937, and received a number of other honors. In recent years he traveled in France, Spain, Belgium, the United States, and other countries, either to attend meetings, or to lecture, and it is the present author's impression that he much enjoyed these travels. Although he took a lead in organizing the recent Faraday Society Discussion in Kingston, Ontario, he could not be encouraged to attend in person. Just before the meeting he was taken ill at his home in Bristol, and a telegram was sent from those present at Kingston to wish him well, but, unfortunately his recovery was of short duration.

D. D. Eley

June, 1961

Contents

1. Chemisorption and Catalysis on Metallic Oxides

BY F. S. STONE

2. Radiation Catalysis

BY R. COEKELBERGS, A. CRUCQ, AND A. FRENNET

3. Polyfunctional Heterogeneous Catalysis

BY PAUL B. WEISZ

4. A New Electron Diffraction Technique, Potentially Applicable to Research in Catalysis

By L. H. Germer

5. The Structure and Analysis of Complex Reaction Systems

By James Wei and Charles D. Prater

6. Catalytic Effects in Isocyanate Reactions

By A. Farkas and G. A. Mills

Chemisorption and Catalysis on Metallic Oxides

F. S. STONE

Department of Physical and Inorganic Chemistry,
University of Bristol, Bristol, England

I. Introduction

The study of the various reactions of carbon monoxide, hydrogen, and oxygen at oxide surfaces holds a particularly important place in the development of research in heterogeneous catalysis. Not only are the well-established technical aspects of these reactions continuously monitored by those engaged in chemical industry, but the chemist interested in fundamental studies of the interaction of gases with oxides naturally turns to the behavior of these gases because of the combination of high reactivity and molecular simplicity which they afford. Finally, for the chemical physicist, they offer a unique opportunity to establish the links between the phenomena of catalysis and the theory of the solid state.

The present article aims to trace the course of research in this field with special reference to the work carried out at Bristol since the establishment by Garner in 1928 of a research group in chemisorption and solid state chemistry. The main emphasis will be on the developments of the postwar period and their counterparts in current research, so it is appropriate in the Introduction to summarize some of the more important results of the early period.

The great technological achievements in catalysis during the first quarter of the century were very largely based on empirical work, and it was not until the period from 1925–1930 that much fundamental research on oxide catalysts began to take shape. Highly significant among the empirical developments of the nineteen-twenties was Patart's discovery of the marked efficiency of a *mixture* of zinc oxide and chromium oxide for the synthesis of methanol, and it was this observation which stimulated Garner to begin a study of the interaction of carbon monoxide and of hydrogen with $ZnO \cdot Cr_2O_3$ and other oxides. This work soon led to the conclusion that these gases could be adsorbed on oxides either "reversibly," in the sense that they could be recovered chemically unchanged on heating the oxide, or "irreversibly," meaning that they could only be recovered on heating as carbon dioxide or water respectively. In the case of $ZnO \cdot Cr_2O_3$, for example, Garner and Kingman (*1*) showed that some of the carbon monoxide or hydrogen taken up at room temperature and low pressure was evolved as such on heating to 100–200°, but was then slowly readsorbed (Fig. 1). On further heating to 350°, the adsorbed gas was recovered as carbon dioxide or water, respectively. An important feature of the work was the study of the heats of adsorption, using a calorimetric technique already initiated some years earlier by Garner and successfully used in his classic studies of oxygen adsorption on charcoal (*2*). By this means it was shown that the heat of adsorption of the "reversibly" adsorbed gas lay in the range between 10 and 30 kcal./mole, establishing that this adsorption was chemical rather than physical in character. It was not, therefore, to be classified with the low temperature adsorptions of hydrogen being discussed at about the same time by Benton and White (*3*) and by Taylor (*4*), which had much lower heats and were physical in nature. Although at the time (1931) the results of Garner and Kingman tended somewhat to obscure the pressing issue of the distinction between physical adsorption and Taylor's "activated" adsorption, their true significance, more readily appreciated in retrospect, is that they were the first clear results to establish the existence of more than one type of chemisorption for reducing gases on oxides.

Later studies by Garner and his co-workers showed that the fraction of carbon monoxide or hydrogen reversibly chemisorbed at room temperature varied from oxide to oxide. Zinc oxide was shown to be a case where the adsorption of carbon monoxide at room temperature was completely reversible. The heat of adsorption, determined both calorimetrically (*5*) and isosterically (*6*), was in the range 12–20 kcal./mole. For several other oxides, however, notably chromia, Mn_2O_3 and $Mn_2O_3 \cdot Cr_2O_3$, the heat of adsorption of carbon monoxide was higher and the chemisorption was irreversible. Moreover, these cases of irreversible chemisorption of carbon monoxide at room temperature were found to leave the surfaces unsaturated with respect to oxygen. The ability to take up oxygen, small in extent when studied before the adsorption of carbon monoxide, was found subsequently to be appreciable. In addition, the amount of oxygen adsorbed after CO treatment corresponded in several cases to one-half the volume of the pre-adsorbed CO.

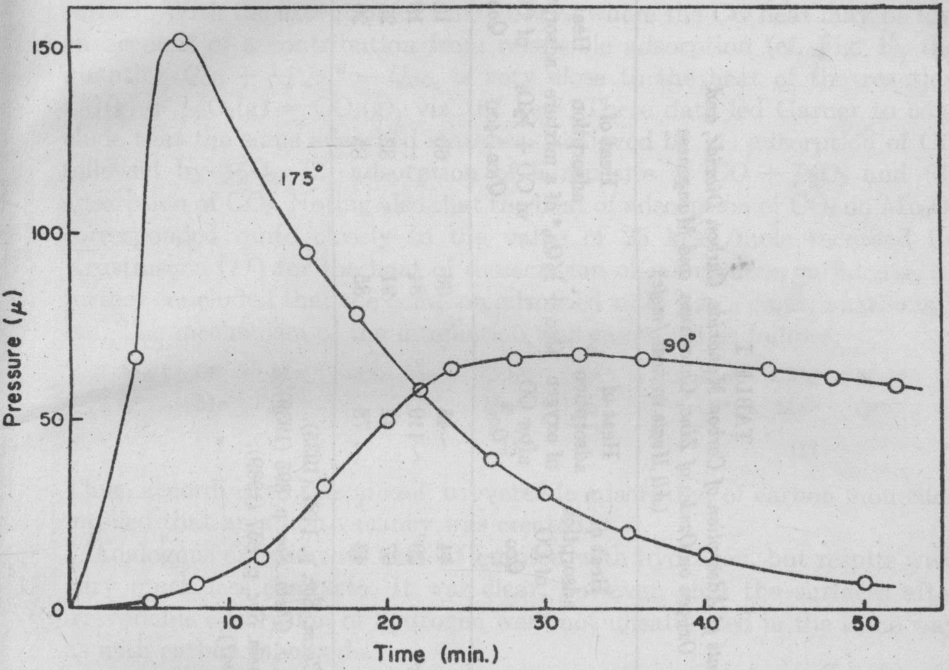

FIG. 1. Desorption and readsorption of hydrogen on $ZnO \cdot Cr_2O_3$.

These interesting observations assumed a more quantitative significance when set alongside the values of the heats of adsorption obtained concurrently with the volumetric measurements. These are summarized in Table

TABLE I

Heats of Adsorption of Carbon Monoxide, Carbon Dioxide, and Oxygen on Oxides of Zinc, Chromium, and Manganese

(All Heats in kcal./mole)

Oxide	Authors	Heat of adsorption of CO Q_{CO}	Heat of adsorption of oxygen after CO $Q_{O_2}^*$	$Q_{CO} + \frac{1}{2}Q_{O_2}^*$	Heat of adsorption of a mixture of $CO + \frac{1}{2}O_2$ $Q_{(CO+\frac{1}{2}O_2)}$	Heat of adsorption of CO_2 Q_{CO_2}	$Q_{CO} + \frac{1}{2}Q_{O_2}^* - Q_{CO_2}$
$ZnO \cdot Cr_2O_3$	Garner and Veal[a]	44	~45	66	66	15	51
Cr_2O_3	Dowden and Garner[b]	29	~110	84	—	18	66
Mn_2O_3	Garner and Ward[c]	67	48	91	82	23	68
$Mn_2O_3 \cdot Cr_2O_3$	Ward[d]	46	78	85	85	20	65

[a] Garner, W. E., and Veal, F. J., *J. Chem. Soc.* p. 1487 (1935).

[b] Dowden, D. A., and Garner, W. E., *J. Chem. Soc.* p. 893 (1939).

[c] Garner, W. E., and Ward, T., *J. Chem. Soc.* p. 857 (1939).

[d] Ward, T., *J. Chem. Soc.* p. 1244 (1947).

I (*7*), where reference is also given to the original papers (*5, 8–10*). Q_{CO} is the heat of adsorption of carbon monoxide on an "oxidized" surface, i.e., one which had been pretreated with oxygen at 450°, evacuated, and cooled to room temperature. $Q_{O_2}{}^*$ is the heat of adsorption liberated when oxygen was subsequently adsorbed, and $Q_{(CO+\frac{1}{2}O_2)}$ the heat liberated per mole of gas taken up when a mixture of $2CO:1O_2$ was admitted to an "oxidized" surface. Note here the agreement with the corresponding $Q_{CO} + \frac{1}{2}Q_{O_2}{}^*$ sum. Q_{CO_2} is the heat of adsorption of CO_2 on an "oxidized" surface. With the exception of $ZnO \cdot Cr_2O_3$, where the CO heat may be low on account of a contribution from reversible adsorption (cf. Fig. 1), the quantity $Q_{CO} + \frac{1}{2}Q_{O_2}{}^* - Q_{CO_2}$ is very close to the heat of the reaction $CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$, viz., 67 kcal. These data led Garner to conclude that the same adsorbed state was achieved by (1) adsorption of CO followed by $\frac{1}{2}O_2$, (2) adsorption of a mixture of $CO + \frac{1}{2}O_2$ and (3) adsorption of CO_2. Noting also that the heat of adsorption of CO_2 on Mn_2O_3 corresponded quite closely to the value of 25 kcal./mole recorded by Krustinsons (*11*) for the heat of dissociation of manganous carbonate, he further concluded that the common adsorbed state was a surface carbonate ion. The mechanism of the interaction was envisaged as follows:

$$\begin{array}{ccccccccccc} Me^{2+} & O^{2-} & Me^{2+} & \xrightarrow{+CO} & Me^{2+} & CO_3^{2-} & Me^{2+} & \xrightarrow{+\frac{1}{2}O_2} & Me^{2+} & CO_3^{2-} & Me^{2+} \\ O^{2-} & Me^{2+} & O^{2-} & & O^{2-} & Me^{2+} & \boxed{2e} & & O^{2-} & Me^{2+} & O^{2-} \\ & \text{I} & & & & \text{II} & & & & \text{III} & \end{array}$$

Thus, according to this model, irreversible adsorption of carbon monoxide implied that an anion vacancy was created.

Analogous experiments were attempted with hydrogen, but results were very much less complete. It was clear, however, that the surfaces after irreversible adsorption of hydrogen were not unsaturated in the same way as with carbon monoxide.

II. The Adsorption and Oxidation of Carbon Monoxide

A. INTRODUCTION

The studies of Garner and his co-workers in the years 1928–1939, which had established the existence of two types of carbon monoxide and hydrogen chemisorption on oxides and which identified "irreversible" chemisorption with incipient reduction, were followed in the immediate postwar period by an intensive study of the properties of copper oxide (*12–15*). The work was later extended to nickel oxide (*16*) and cobalt oxide (*17, 18*). With each of these oxides it was established that carbon monoxide was capable of reacting not only with lattice oxygen, but also with adsorbed oxygen. The concept of irreversible chemisorption involving a carbonate ion and ultimate reduction remains an acceptable explanation of the facts for the interaction of CO with the oxides at temperatures above 100–200°, but at room temperature other processes are to be distinguished. It is the purpose of this section to describe the purely chemical aspects of this work and to illustrate their bearing on the catalytic oxidation of carbon monoxide at low temperatures. The research as a whole provides a detailed example of the classical approach in heterogeneous catalysis to the fundamental problem of correlating catalytic activity with the stability of adsorbed species.

B. Heats of Adsorption and Complex Formation

Most of the work to be discussed in this section has been carried out on oxide films about 100A. in thickness present on a base of underlying metal. The parent metal has first been formed as granules by processes designed to minimize the oxide content. Copper was prepared by the reduction of an aqueous suspension of copper hydroxide with hydrazine. Nickel and cobalt were prepared in the vacuum system by thermal decomposition of nickel oxalate and cobalt formate, respectively. The metals have then been reduced *in situ* with hydrogen. Finally the oxide film has been prepared by controlled oxidation, usually at low pressure. The surface areas of the oxides lay in the range between 1 and 10 m.^{2}/g. With the exception of one calorimeter containing oxidized copper foil (*13*), heats of adsorption have been measured using calorimeters of Type 1f described by Garner and Veal (*19*). A typical heat liberation of 0.5 calorie, corresponding, for example, to the adsorption of 0.5 cm.^{3} of a gas with a heat of adsorption of 22.4 kcal./mole, could be measured to an accuracy of 1%. The method of using an oxide film on a metal base had two important advantages. First, it enabled the oxide surface to be cleaned more readily after exposure to oxygen. Oxygen, sometimes difficult to desorb on baking out, was in the present case simply incorporated into the oxide film at the expense of some underlying metal. After studies of CO adsorption, outgassing may be accompanied by some reduction of the surface: in such cases oxygen has to be admitted to the oxide to replenish the surface. It is obviously important to be able to remove the oxygen remaining as a chemisorbed film, and some of the earlier studies (see Section 1) were open to objection on these grounds. The second advantage came in the adsorption calorimetry. The high thermal conductivity of the oxide-coated granules (relative to pure oxide) assisted heat distribution within the catalyst mass.

We begin with a discussion of results obtained on copper (cuprous) oxide. Magnetic studies (*20*) have confirmed that the method of preparation yielded only cuprous oxide. On a surface free from adsorbed oxygen, carbon monoxide could be adsorbed reversibly at 20°. If, however, oxygen had been preadsorbed at 20°, the rapid adsorption of carbon monoxide