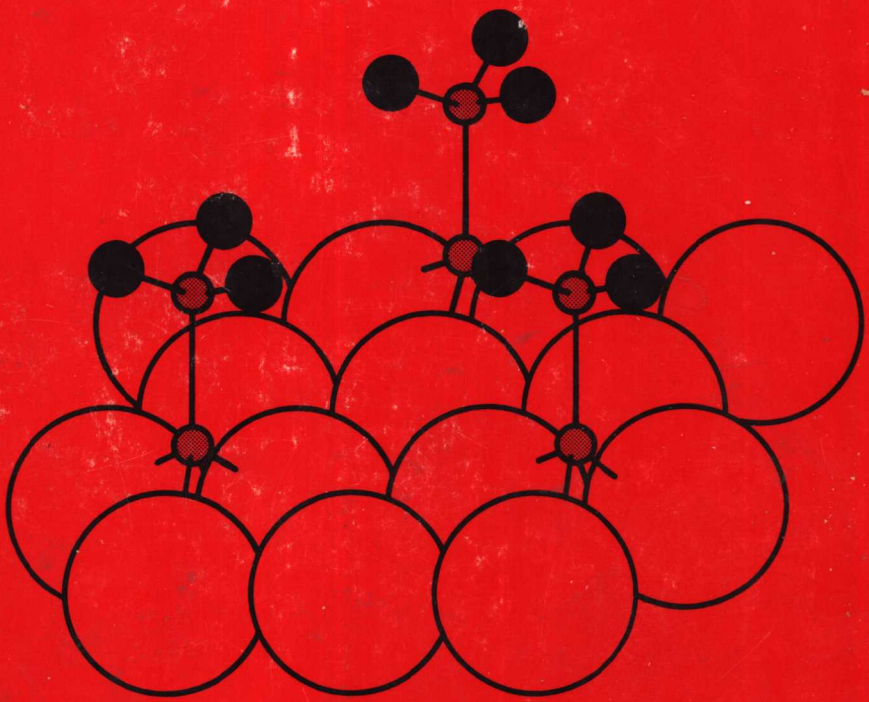
Heterogeneous Catalysis

Proceedings of the Second Symposium
of the
Industry-University Cooperative Chemistry Program
of the
Department of Chemistry, Texas A&M University
April 1–4, 1984

Editor

Bernard L. Shapiro



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Professor of Chemistry
Texas A&M University
College Station, Texas
U.S.A.

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Organometallic Compounds

Foreword

On Sunday evening, April 1, 1984, approximately 150 industrial and university scientists, graduate students, and postdoctoral fellows assembled to enjoy refreshments, conversation, and a string duo. This gathering marked the beginning of the second annual Industry-University Cooperative Chemistry Program Research Symposium. This year as last, an outstanding group of speakers was on hand to present the results of their latest research. In addition, nineteen posters were exhibited at a wine and cheese party on Monday evening, April 2.

Our purpose — to bring together industrial and university scientists in a relatively informal and relaxed setting -- was well served by this conference, for an excellent exchange of ideas and information was evident throughout the

program. Especially important was the interaction of graduate students with industrial scientists and invited speakers.

I would like to thank Jack Lunsford and Mike Rosynek for their skill in planning the scientific program and co-chairing the symposium. Thanks are also due to Elizabeth Porter, my intrepid and capable administrative assistant, who arranged all the social events, advertising, mailing, and much more. Graduate student Pat Tooley supervised our volunteer staff of graduate students who provided transportation, registration, and generally saw to our needs.

Special thanks go to our editor, Barry Shapiro, who, when the conference is finished, doggedly pursues our speakers for manuscripts and forges them into the fine volume you see here. Russel Kirk and Marilyn Hollar did their usual excellent job of formatting some of the chapters, preparing the front and back matter, and handling the many detailed steps involved in integrating the chapters into a complete, professional appearing book.

Finally, both Dr. Shapiro and I wish to acknowledge the exemplary cooperation and efficiency which have again characterized our interactions with the staff of the Texas A&M University Press.

These IUCCP Research Symposia, the Proceedings volumes, and indeed, the entire IUCCP program itself, are possible

only through the sponsorship of our industrial affiliates. It is thus an especial pleasure to acknowledge their generous support, both tangible and intangible. The names of our sponsor companies appear below.

Planning for next year's symposium, "New Directions in Chemical Analysis," is already underway.

College Station, Texas
June 1984

Abraham Clearfield

Professor of Chemistry
Director, Industry-University
Cooperative Chemistry Program

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Preface

One of the objectives of the IUCCP is to promote the exchange of scientific information between academic and industrial scientists. Since heterogeneous catalysis is a subject of immense importance in the chemical and refining industries, it was a logical topic for the 1984 IUCCP Symposium. Fifteen invited papers were presented in the general areas of novel catalytic materials, shape-selective catalysis, oxidation catalysis, CO/H_2 catalysis, and experimental techniques. Of the fifteen speakers, four were from industrial laboratories, nine were from academic institutions, one was from a national laboratory, and another was from a research institute. Two-thirds of the symposium attendees were from industrial laboratories. Thus, there was ample opportunity for information exchange between the various groups of participants, and, in the opinion of the organizers, the Symposium attained this objective very effectively.

Through the publication of the papers presented at the Symposium, this valuable scientific information is made available to the greater community of catalytic chemists and engineers. All of us who reap the benefits of this research are indebted to the authors, who have achieved an excellent balance between literature review and the presentation of exciting new results. It is hoped that future research in both applied and fundamental catalysis will be stimulated through the Symposium and this Proceedings volume.

College Station, Texas
June 1984

Jack H. Lunsford
Professor of Chemistry

Michael P. Rosynek
Associate Professor of Chemistry

Co-Chairmen, 1984 IUCCP
Research Symposium

Contents

Catalysis by Oxide-Supported Metal Clusters

B. C. Gates

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, U.S.A.

Abstract

Metal clusters react with functional groups of metal oxides such as silica and alumina to give supported metals having "molecular" structures. For example, reaction of $Os_3(CO)_{12}$ with surface -OH groups gives $HOs_3(CO)_{10}$-O-Al≡, and reaction of $H_4Os_4(CO)_{12}$ with basic surface groups gives $[H_3Os_4(CO)_{12}]^-$Al≡. The surface-bound clusters have been observed by electron microscopy and characterized by a variety of spectroscopic techniques. Most of these clusters are relatively unstable, undergoing fragmentation to give smaller clusters, mononuclear complexes, and aggregated metal. Intact osmium clusters are catalytically active for olefin isomerization at temperatures $\leq 100^{\circ}C$. Clusters of osmium, ruthenium, and cobalt are also

present on the surfaces of CO hydrogenation catalysts used under typical Fischer-Trospch conditions, but their role in catalysis remains to be elucidated.

Introduction

Supported metals used as industrial catalysts typically consist of aggregates or crystallites of various sizes, shapes, and (for many reactions) catalytic activities. The nonuniformity of these materials hinders the determination of relations between structure and catalytic performance. Such relations may be determined more straightforwardly with simpler metal structures: single crystals can be used with the methods of surface science to determine catalytic characteristics of different exposed crystal planes; alternatively, molecular analogs anchored to supports can be prepared and characterized with the methods of organometallic chemistry applied to surfaces.

Mononuclear complexes of metal ions bonded to surfaces are a well-developed class of catalysts (1), including silica-supported chromocene and the related materials used on a large scale in polymerization of

α-olefins. Polynuclear metal complexes (metal clusters) bonded to supports, on the other hand, are a newly developed class of materials with few known examples. They offer intriguing possibilities as catalysts: like surfaces, they offer neighboring metal centers, and like organometallic complexes used in solution, they offer unique (molecular) structures; the size (nuclearity) and composition of the metal framework and the ligand environment can all be viewed as potential variables for catalyst design. However, most metal clusters (in solution or on supports) are lacking in stability and difficult to work with.

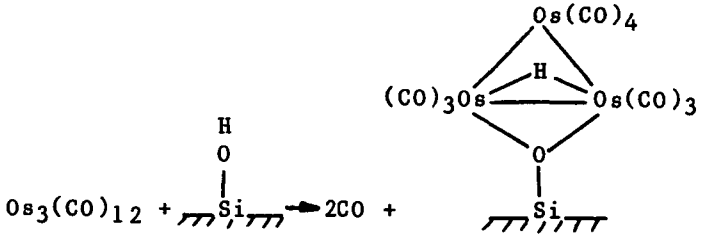
The objective of this review is to summarize and assess the literature of metal clusters supported on simple metal oxides such as silica and alumina. Most of the reported work is concerned with osmium clusters having relatively robust metal frameworks, especially triosmium. There is a closely related literature of metal clusters supported on functionalized metal oxides and polymers, which is reviewed elsewhere (2).

Synthesis of Oxide-Supported Metal Clusters

The reported syntheses have been inferred (or,

more typically, rationalized) on the basis of the functional group chemistry of the oxide supports and the known organometallic chemistry of the metal-cluster precursors. Often mixtures of surface species have been formed as a result of the reaction of organometallics with oxide surfaces; only the syntheses giving relatively well-defined surface structures are cited here.

The few examples of oxide-supported clusters with well-defined structures are listed in Table 1, the most thoroughly investigated of them being neutral triosmium clusters on SiO_2 and Al_2O_3, first described by Ugo and Basset and coworkers in 1979 (3,4). The synthesis is formally described as an oxidative addition involving $Os_3(CO)_{12}$ and a surface -OH group:



(1)

The stoichiometry was established by measurement of CO evolution (4). The reaction can be reversed in the