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# Catalysis and Surface Properties of Liquid Metals and Alloys

Yoshisada Ogino

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**Yoshisada Ogino**

*Department of Chemical Engineering  
Tohoku University  
Aramaki-Aoba, Sendai, Japan*

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## Preface

The primary intention of this book is to present up-to-date information about the catalysis and surface properties of liquid metals and liquid alloys. This book is intended for use by chemical engineers and researchers in catalysis, surface science, liquid metals, and chemical process technologies. Although several excellent monographs are available for those readers interested in the bulk properties of liquid metals and alloys, there is no other book that integrates information about their surface phenomena. Publication of this book, I believe, improves our understanding of the science and technology of liquid metals and alloys.

The catalytic properties of liquid metals and alloys are reviewed in the first four chapters. The substance of these chapters has been taken mainly from research carried out in my laboratory, because of the lack of published research by other authors. Thus, it is hoped that the information presented about experimental techniques and surface catalysis will be especially useful for those readers interested in working with liquid metals and liquid alloys. A mechanistic account of catalysis at the atomic, or electronic, level is presented in Chapter 4. The problems treated in this chapter address the structures and properties of liquid metals.

The last three chapters review the recent advances in research on the surface properties of liquid metals and alloys. The discussion covers much of the literature from 1970 through 1985. Experimental data are summarized in tables as much as possible. I would like to express my great respect to all authors who have contributed the valuable scientific information cited in this book.

Although mathematical expressions have been minimized throughout this book, this never means that rigorous theoretical treatments are unimportant. Theoretical treatments give the reader easy access to the essential knowledge accumulated in this particular field of science. To understand the present situation regarding the theory of liquid metals, readers should consult J. M. Ziman, *The Physics of Metals. 1. Electrons* (Cambridge, 1969); T. E. Faber, *An Introduction to the Theory of Liquid Metals* (Cambridge, 1972); or M. Shimoji, *Liquid Metals* (Academic Press, 1977). For readers who wish to study the theory of surface tension, the book by C. A. Croxton, *Statistical Mechanics of the Liquid Surface* (John Wiley & Sons, 1980), is recommended.

For myself, this book is a professional milestone. Thus, I express my thanks to Dr. Maurits Dekker, Marcel Dekker, Inc. who kindly recommended that I publish this book; to Carol Mayhew and Henry Boehm, editors at Marcel Dekker, Inc; for their patience and valuable advice; to Dr. Yasukatsu Tamai (Emeritus Professor, Tohoku University) for his constant encouragement; and to Dr. Sentaro Ozawa for his illustrations. I gratefully acknowledge the Ministry of Education, Science, and Culture of Japan for its constant financial support to the study on catalysis of liquid metals. I also wish to thank my family, in particular my wife Hisako, for their forbearance and hearty help during the preparation of the manuscript.

Finally, I express my sincere personal acknowledgment to the late Dr. Hiroshi Uchida, to whom this book is dedicated.

Yoshisada Ogino

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# 1

## History and Scope

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### I. INTRODUCTION

In this chapter important earlier research related to liquid metal catalysis and its scientific background will be described first, in order to clarify the roles played by this work in advancing the study of heterogeneous catalysis. Then the author's motive for initiating and promoting systematic studies on liquid metal catalysis will be described. The purpose of this chapter is to describe the scientific foresight of earlier researchers and to evaluate the position of the work of the author and his co-workers in the history of the catalysis research.

## II. HISTORICAL SURVEY

This survey begins with Ipatiew's work which was published in the beginning of this century (1901) [1]. He found that metallic zinc catalyzed the decomposition of alcohols, even above its melting point. Although metallic zinc does not always liquefy at the melting point when it is covered by an oxide layer, Ipatiew's finding is sufficient to suggest that the catalyst metal might possess a catalytic activity, even in its liquefied state. However, Ipatiew gave no special attention to the catalytic activity of liquid metal, and thus 20 years or more elapsed without any significant advances in the research on the catalysis of liquid metal.

In 1925 Taylor [2] published the concept of active centers, which greatly stimulated catalysis researchers and brought about intensive controversy. Several workers postulated that the active centers, areas with special structures, would disappear on fusion and therefore the catalytic activity of a solid metal would disappear or change drastically at the melting point. Thus, they measured the activities of metals below and above the melting points. For instance, Hartman and Brown [3] found that the nitrobenzene hydrogenating activity of a supported cadmium (Cd) catalyst exhibited a maximum at the melting point of Cd (320.9°C) (Fig. 1a), which supported Taylor's opinion. Steacie and Elkin [4] argued against this and considered that Hartman's data merely indicated a reduction in the degree of dispersion of Cd particles on the surface of the catalyst support. Steacie asserted that a pure metal, instead of a supported metal, had to be used as a catalyst to investigate the validity of the concept of active centers. Thus, he employed metallic zinc as a catalyst for the methanol decomposition reaction and found that no discontinuous changes in the catalytic activity took place at the melting point of zinc (419.5°C) (Fig. 1b). However, Adadurov and Didenko [5] suspected that the catalytic activity observed by

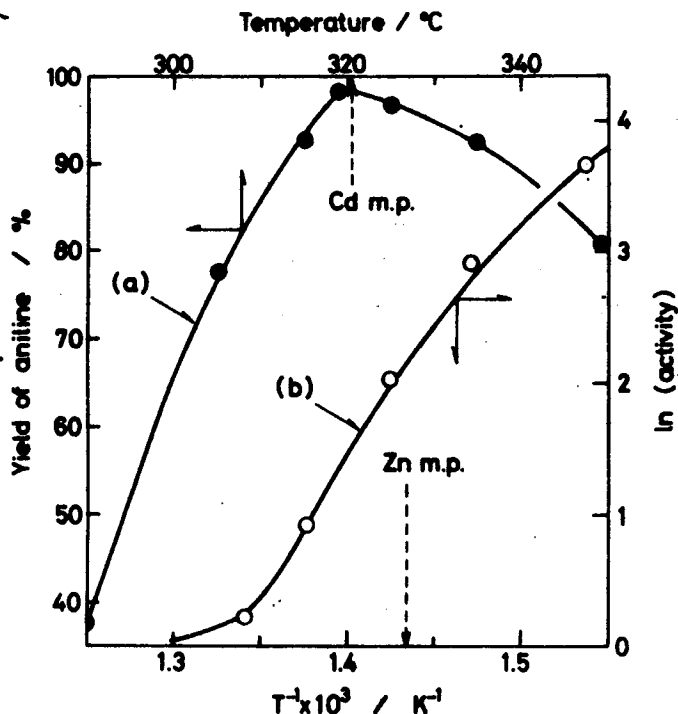


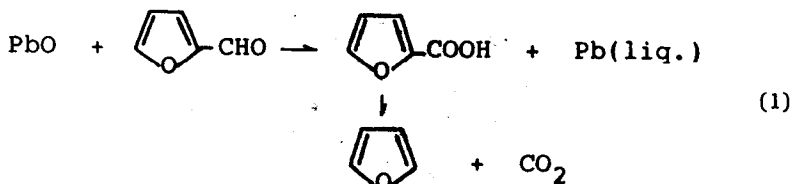
Fig. 1 Temperature dependence of catalytic activities. (a) Nitrobenzene hydrogenating activity of a supported Cd catalyst [3]; (b) methanol decomposition activity of a metallic zinc catalyst [4].

Steacie might be the activity of the oxide layer covering the surface of metallic zinc. Schwab and Martin [6] also argued against Steacie's result and showed that pure zinc liquid was inactive and that only the liquid zinc contaminated by oxygen was active.

Although Weller and his co-workers [7] examined liquid tin  $\text{Sn}(\text{liq.})$  as a coal liquefaction catalyst, little work on the catalysis of liquid metal had been done until 1960 when Schwab [8,9] published his work on catalysis by liquid alloys. He measured the rate of decomposition of formic acid over two series

of liquid alloys (Hg-based binary alloys and Tl-based binary alloys) and interpreted the experimental results on the basis of the electron theory of metals. Unfortunately, however, information about the electronic properties of liquid metals and liquid alloys was not sufficient for his purpose, and he had to use the electron theory of alloys in the solid state. In addition, Schwab confined himself to the study of formic acid decomposition. Therefore, various aspects characterizing the catalysis of liquid metals and liquid alloys remained to be discovered.

To the author's knowledge, no industrial use of the liquid metal catalyst has been realized, although a few patents [10] have claimed the use of a liquid metal catalyst in petroleum decomposition. In this connection, Meszaros's report [11] is cited here. He reported the use of a "melt bed reactor" in producing furan from furfural:



In the upper half of this reaction, furfural reacts with PbO and produces furan and Pb(liq.), which goes down toward the bottom of the reactor. In the lower part of the reactor, the Pb(liq.) is oxidized by air and rises due to buoyancy toward the reaction zone. Clearly the reaction of lead is cyclic but not catalytic.

### III. MOTIVE FOR STUDYING THE CATALYSIS OF LIQUID METAL

It is easy to suppose that studies of the catalysis of liquid metals would have the following advantages.

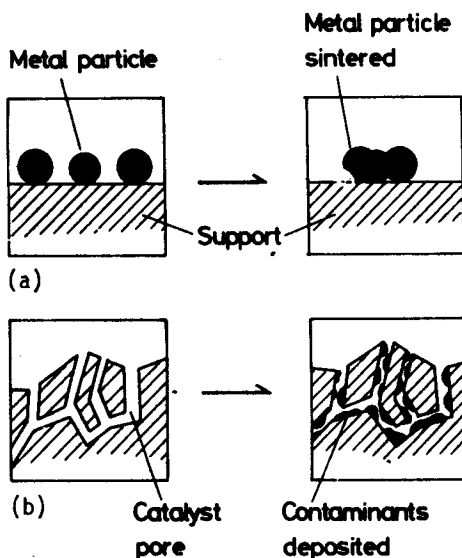


Fig. 2 Models for typical deactivation processes of catalysts: (a) sintering, (b) fouling.

1. No sophisticated techniques are required in preparing the catalyst, although precautions against impurities and contaminations of the catalyst metal are necessary.
2. The deactivation due to sintering (Fig. 2) never takes place.
3. Carbonaceous materials formed by side-reactions are automatically separated from the bulk of the liquid metal due to buoyancy and therefore the deactivation due to the catalyst fouling can be avoided by the use of an appropriate reactor; a catalyst fouling as illustrated in Fig. 2 would never take place.

Thus, the experimental data will be reproducible and universal, and they will provide a firm basis to the scientific discussion on surface catalysis.



5. I. E. Adadurov and P. D. Didenko, *J. Amer. Chem. Soc.*, **57**, 2718 (1935).
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12. Y. Ogino, *Catal. Rev.-Sci. Eng.*, **23**, 505 (1981).

# Techniques for Measuring Catalytic Activity

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## I. INTRODUCTION

Activity measurement is one of the most fundamental experiments in catalysis research and the methodology for measuring activities of solid state catalysts is almost completely established. In contrast to this, the activity measurement itself has been a problem to be solved by a number of trials and experiences in the research of the liquid metal catalysis. The problem has only partly been solved and hence the situation mentioned above



is still continuing. Thus, most of the experimental methods that will be described in this chapter will probably need further refinement.

## II. CATALYST PURIFICATION

Although most of the catalyst metals with high purity are commercially obtainable, purification using the technique illustrated in Fig. 1 [1] is recommended, even in an ordinary activity test. The raw metal, charged in a catalyst preparatory tube, is heated well beyond its melting point and then purified hydrogen is passed through. The oxide of the catalyst metal is either reduced or separated, together with other contaminants, from the bulk of the liquid metal by buoyancy. Then the direction of the hydrogen stream is reversed, causing a transfer of the liquid metal from the catalyst preparatory tube to the reactor. The hydrogen pressure is so controlled that only a pure portion of the liquid metal can be taken into the reactor. Finally, the pipeline connecting the preparatory tube and the reactor is sealed by fusion. The preparation of a liquid alloy [2] is carried out in a manner similar to that mentioned above. For the catalyst purification mentioned above, at least a hydrogen purification device is necessary. Additional connections

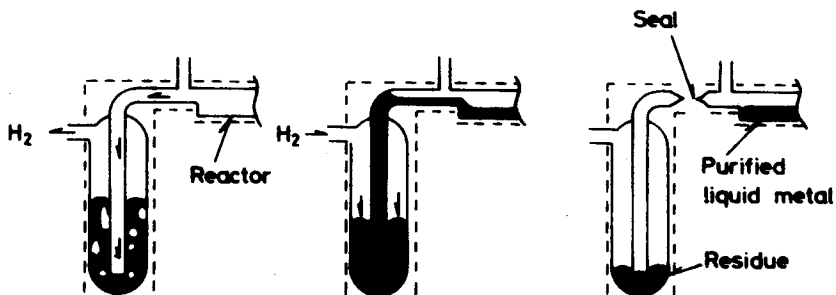


Fig. 1 Procedures for catalyst purification.