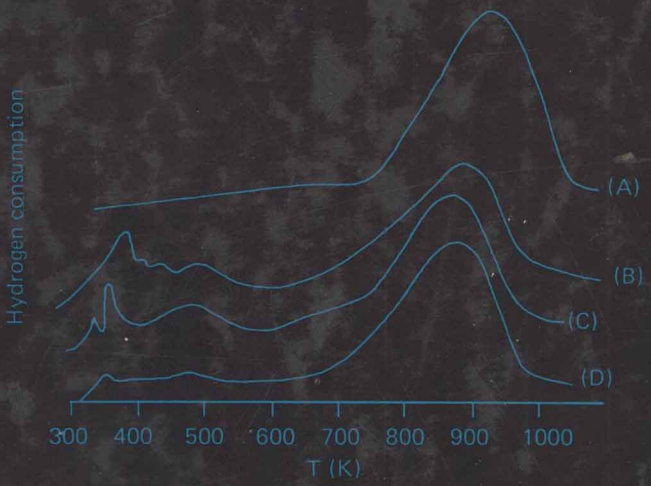
CHEMICAL INDUSTRIES/24

TEMPERATURE-PROGRAMMED REDUCTION FOR SOLID MATERIALS CHARACTERIZATION



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Temperature-Programmed Reduction for Solid Materials Characterization

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PREFACE

Temperature-programmed reduction (TPR) is a relatively new technique used for the characterization of solid materials. Since the first publication in this area (1975), many papers have appeared in the literature that have shown its applicability in a variety of scientific fields, most particularly in characterization of catalysts. In 1982 the first review on the subject of TPR appeared in *Catalysis Reviews.*

The technique, based on the reducibility of species in solids, enables one to obtain information not only of a purely analytical nature but also, and more importantly, about the condition of species present in and on solids. At the same time, the technique is relatively simple in concept and application. It involves very low capital investment relative to more sophisticated techniques used in the above area.

As a result, TPR and related techniques are now becoming commonly used weapons in the scientist's armory for the characterization of solids. This applies across the whole spectrum of academic and industrial research. It is thus timely that the first book should appear that represents not only the state of the art of the technique, but also recent developments and future trends.

The book is intended as an informative guide to both experts and initiates in the field. The principles and theory of isothermal and dynamic reducibility (TPR) are discussed in full detail, together with a clear description of the parametric sensitivity of the technique (Chapter 2). Chapter 3 describes the instrumentation that has been used for the measurement of TPR. Chapter 4 fully discusses the areas where the technique has found application in such a way that the reader should gain ready knowledge of the current state of the art and the possible advantages and disadvantages of the technique in comparison with other techniques. Finally, in Chapter 5 the developing trends in temperature programming are discussed. Here we are concerned with not only TPR but temperature-programmed reactions in general. This chapter attempts to point the direction in which temperature-programming techniques for the characterization of materials are heading.

This volume is aimed at a wide audience, including academics (undergraduate, postgraduate and university staff), research scientists, and technologists in industry and research institutes concerned with the manifold problems involving characterization of solids in such fields as heterogeneous catalysis, materials science/metallurgy, and analytical chemistry.

The terminology used in this and related fields has led to some confusion; in particular, the acronym TPR has been used to refer to both temperature-programmed reduction and temperature-programmed reaction. We would recommend and have used throughout this work the abbreviation TPR to refer to temperature-programmed reduction. Where reference is made to

temperature-programmed reaction the expression is written in full. Abbreviations relating to specific temperature-programmed reactions present, so far, no ambiguity and we have recommended the following:

Temperature-programmed oxidation (TPO)

Temperature-programmed sulfidation (TPS)

Temperature-programmed carburization (TPC)

Temperature-programmed methanation (TPM)

We would like to thank Drs. S. J. Gentry and N. W. Hurst of the Health and Safety Executive, who have done much pioneering in this field and did much of the groundwork necessary for the preparation of this work. We have drawn freely from the original review article, of which they were coauthors, in the preparation of this book. We would also like to thank Mr. I. Kitchener of the London Research Station of British Gas for providing us with advice on optimizing conditions for TPR. Finally, thanks are due to all the scientists who provided details of their work for inclusion in the book and permission to reproduce diagrams.

Alan Jones

Brian McNicol

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I. BACKGROUND

Temperature-programmed reduction (commonly abbreviated to TPR) is a technique used for the chemical characterization of solids. The essence of the technique is the reduction of a solid by a gas at the same time that the temperature of the system is changed in a predetermined way. Chemical information is derived from a record of the analysis of the gaseous products.

In the most commonly encountered apparatus, the solid is reduced by flowing hydrogen, the concentration of which is monitored downstream of the reactor. Provided that reduction has taken place over the temperature excursion of the reactor, the analysis record is simply the hydrogen consumption and is usually displayed as a function of the temperature of the reactor.

A typical reduction profile, as shown in Fig. 1, consists of a series of peaks. Each peak represents a distinct reduction process involving a particular chemical component of the solid. The position of a peak in the profile is determined by the chemical nature and environment of the chemical component, and the area of the peak reflects the concentration of that component present in the solid.

TPR is a relatively new technique for characterizing solids. It is highly sensitive and does not depend on any specific property of the solid under investigation other than its reducibility. The technique was first investigated about 13 years ago by Jenkins [1] during a study of catalysts using the temperature-programmed desorption technique pioneered by Cvetanovic and Amenomiya [2]. Jenkins realized that valuable information could be obtained from the reduction pretreatment stage of this technique if the reduction was also performed in the temperature-programmed mode. A series of experiments provided data which, together with information from other techniques, enabled the catalysts to be fully characterized.

The technique was soon exploited by others, and a notable early study [3] was made using the technique to characterize a series of solid catalysts of noble metals supported on refractory oxides. Over the last decade the technique has been exploited and developed considerably by workers around the world to the extent that TPR now has a place alongside other techniques for the characterization of solids, and in 1982 the first review article on the subject was published [4].

The technique can be regarded as the principal member of a family of temperature-programmed reaction techniques. Its

status as principal member is only due to the fact that the reduction reaction has attracted the most attention from researchers. In principle, valuable information can be obtained by investigating many different types of chemical reactions in a temperature-programmed mode. Using the same or similar apparatus, temperature-programmed oxidations, methanations, sulfidations, and carburizations have been reported.

On the basis of the type of information it can provide, the TPR technique can be classified with the spectroscopic and X-ray techniques that have been traditionally and indeed are currently used to characterize solids. Almost all of these techniques impose severe requirements on the solid or on the conditions under which it can be investigated. These requirements necessarily limit the information that can be obtained and the range

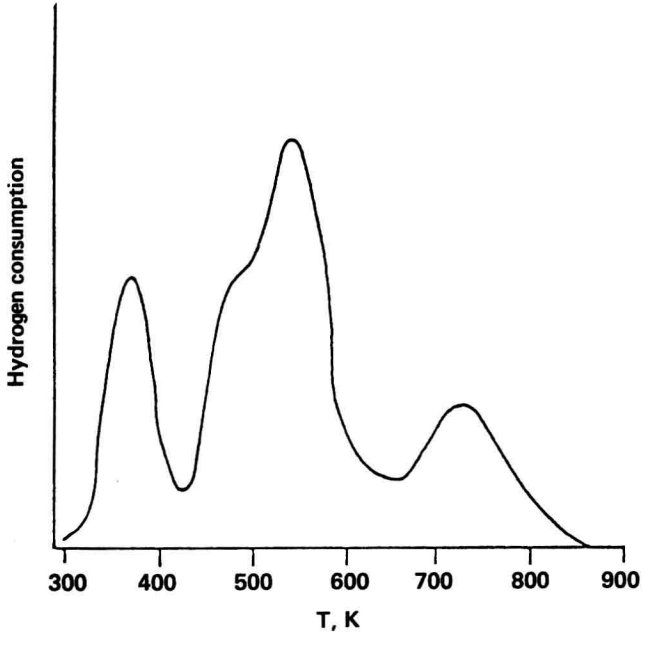

Fig. 1 A typical reduction profile.

of solids that can be investigated. The TPR technique, while capable of providing chemical information similar to that from the other techniques, has, in general, a much wider range of application. Even the condition that the solid must be reducible is not mandatory, since valuable information has been obtained on *reduced* solids using TPR by first mildly oxidizing the solids and then subjecting them to the TPR experiment.

In another sense, and certainly on the grounds of similarity of experimental procedure, TPR can be classified with a broad range of techniques, known as thermoanalytical techniques, that are used to generate physical and chemical information on solids [5]. In general, these techniques depend on the measurement of a parameter of a physical or chemical property of a solid as the temperature of the solid is varied, as for TPR, in a predetermined manner. Figure 2 presents a classification of the principal techniques. These techniques provide information on a wide range of phenomena from the purely physical to the totally chemical [5]. Temperature-programmed desorption (TPD) is included in Fig. 2 under techniques dependent on the evolution of "volatiles" since there are broad experimental similarities with evolved gas analysis (EGA) and both techniques can give information on the physical desorption of gases as well as on gases evolved by chemical mechanisms. Temperature-programmed reduction, along with the other temperature programmed reaction techniques, is thus identified as a more chemically based technique concerned with analysis of gases from purely chemical processes.

Temperature-programmed reduction profiles of complex solids can show a great deal of detail, reflecting complex reduction processes. The use of such profiles as "fingerprints" to provide a rapid assessment of the correctness of the composition of a solid has proved useful in many applications. In particular, the fingerprint temperature reduction profile has found application as a tool for quality control in the preparation of industrial catalysts.

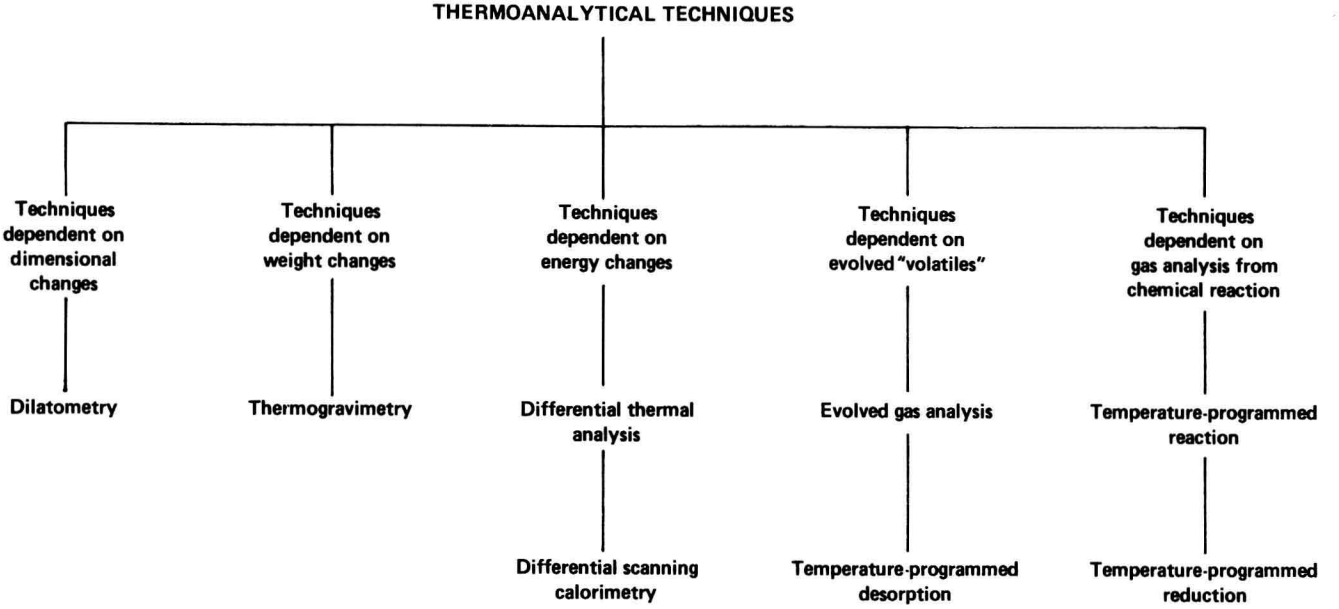

Fig. 2 A classification of thermoanalytical techniques.

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