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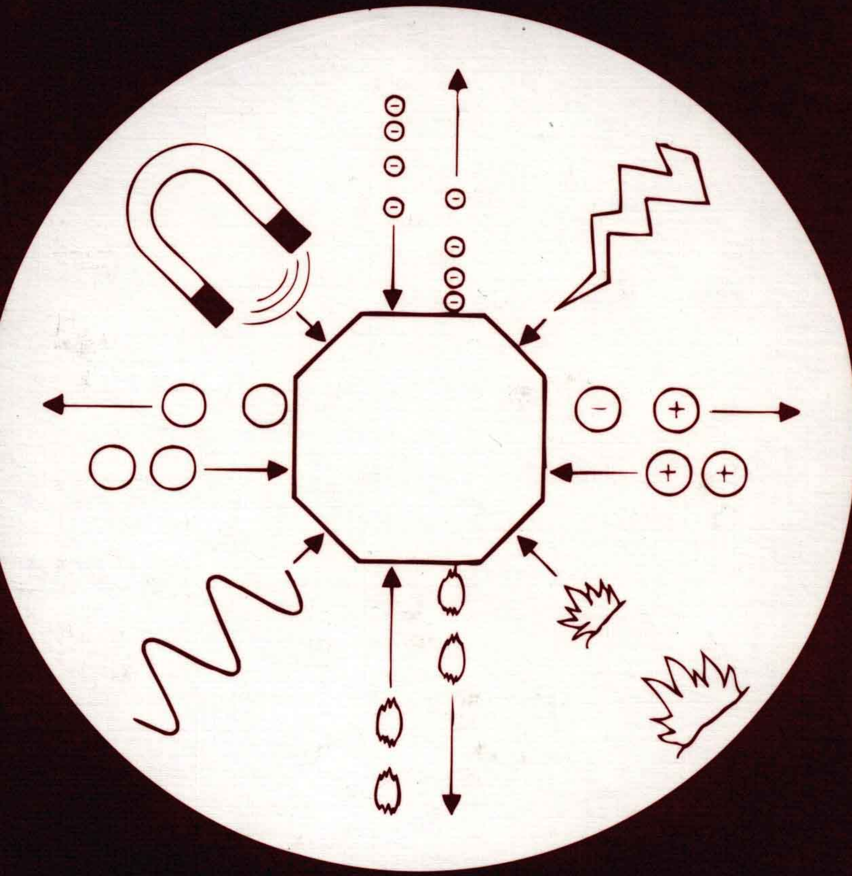

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CATALYST DEACTIVATION 1994

B. Delmon
G.F. Froment
(editors)

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CATALYST DEACTIVATION 1994

Proceedings of the 6th International Symposium, Ostend (Belgium), October 3-5, 1994

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CATALYST DEACTIVATION 1994

PREFACE

We are proud to present the Proceedings of the 6th International Symposium on Catalyst Deactivation held in Ostend, Belgium from October 3 to 5, 1994. This symposium is a continuation of the series of symposia on Catalyst Deactivation held in Berkeley, 1978; Antwerp, 1980; Berkeley, 1985; Antwerp 1987 and Evanston, 1991. It is also an activity of the Working Party "Chemical Engineering in the Applications of Catalysis" of the European Federation of Chemical Engineering.

The objective of the symposium is to promote a scientific approach of the phenomenon of catalyst deactivation which will contribute to the development of catalysts less subject to structural transformations and more resistant to poisons and coke formation.

These aspects are dealt with in 12 plenary lectures, 48 oral communications and 35 posters, critically selected from an impressive response to the call for papers.

It is rewarding that both fundamental and applied aspects are dealt with. The deactivation of catalysts in important industrial processes like fluid bed catalytic cracking, hydrotreatment, hydrodesulfurization, catalytic reforming, hydrodenitrogenation, steam reforming, hydrodemetallization, hydrocracking, Fischer-Tropsch synthesis, propane dehydrogenation, phtalic anhydride synthesis receives considerable attention. Mechanisms of poisoning, sintering and coking are further investigated and modeled. New experimental techniques for the characterization and the quantification of the deactivation are also introduced.

Finally, the international character of the symposium is truly impressive : the papers originated from some 30 countries.

May these Proceedings, like the Symposium itself, contribute to the continued development of this field of research and to the promotion of contacts between academic and industrial investigators. We hope that it will be a fertile basis for the 7th International Symposium on Catalyst Deactivation.

B. Delmon
G.F. Froment
Chairmen

Catalyst Deactivation 1994 was organized by : **The Technological Institute of the Royal Flemish Society of Engineers (TI-K VIV)**

The K VIV is the professional organization of the academically trained Flemish engineers. It represents more than 11.000 members.

In 1940 the Society founded the Technological Institute, with the aim of disseminating information on scientific and technological development by means of seminars, lectures, courses, congresses, conferences.

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Sintering Kinetics of Supported Metals: Perspectives from a Generalized Power Law Approach

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Studies of sintering kinetics of conventional supported metal catalysts are reviewed. Available kinetic data for sintering have been reanalyzed using the new General Power Law Expression (GPLE), which provides the capability of treating these data in a consistent, unifying fashion such that quantitative comparisons regarding effects of reaction conditions and catalyst properties are possible for the first time. It is shown that all available dispersion versus time data can be fitted to second order GPL kinetics. From the analysis of these data new conclusions arise regarding the effects of atmosphere, time, temperature, support, promoters, and metal on the thermal stability of supported metals.

1. INTRODUCTION

Sintering is an important mode of deactivation in supported metals. The high surface area support (carrier or substrate) in these catalysts serves several functions: (1) to increase the dispersion and utilization of the catalytic metal phase, (2) to physically separate metal crystallites and to bind them to its surface, thereby enhancing their thermal stability towards agglomeration, and (3) in some cases to modify the catalytic properties of the metal and/or provide separate catalytic functions. The second function is key to the prevention or inhibition of thermal degradation of the catalytically active metal phase.

Thermally induced deactivation of catalysts is a particularly difficult problem in high-temperature catalytic reactions. Thermal deactivation may result from one or a combination of the following: (i) loss of catalytic surface area due to crystallite growth of the catalytic phase, (ii) loss of support area due to support collapse, (iii) reactions/transformations of catalytic phases to noncatalytic phases, and/or (iv) loss of active material by vaporization or volatilization. The first two processes are typically referred to as "sintering." Sintering, solid-state reactions, and vaporization processes generally take place at high reaction temperatures (e.g. > 500°C), and their rates depend upon temperature, reaction atmosphere, and catalyst formulation. While one of these processes may dominate under specific conditions in specified catalyst systems, more often than not, they occur simultaneously and are coupled processes.

Sintering of supported metals involves complex physical and chemical phenomena including dissociation/emission of metal atoms from crystallites, diffusion of atoms and crystallites across support surfaces, spreading of particles, wetting of the support by particles, nucleation of particles, coalescence and/or bridging of two particles, capture of atoms by particles, liquid formation, vaporization of metal atoms, and volatilization of metals as complexes. The importance of these different processes may change with reaction condition (especially temperature), time, and catalyst formulation (e.g support and/or promoter). The treatment of sintering processes requires an understanding of surface diffusional processes, interfacial phenomena, solid-state reactions and the energetics of metal-metal and metal surface interactions. Most of these processes are only qualitatively understood. Accordingly, the investigation and simulation of sintering phenomena are difficult tasks. Moreover, thermal deactivation problems are generally more difficult to prevent and to reverse than other deactivation problems such as poisoning and carbon deposition.

Nevertheless, efforts to understand, treat, and model sintering/thermal-deactivation phenomena are easily justified. Indeed, deactivation considerations greatly influence research, development, design, and operation of commercial processes. While catalyst deactivation by sintering is inevitable for many processes, some of its immediate, drastic consequences may be avoided or postponed. If sintering rates and mechanisms are known even approximately, it may be possible to find conditions or catalyst formulations that minimize thermal deactivation. Moreover, it may be possible under selected circumstances to reverse the sintering process through redispersion (the increase in catalytic surface area due to crystallite division or vapor transport followed by redeposition).

Studies of sintering and redispersion of supported metal catalysts have been reviewed by several authors [1-18]; most of these reviews focus on early kinetic studies of sintering of supported metal catalysts using a simplified power law expression (SPLE). Unfortunately this crude approach does not permit sintering kinetics to be presented in a consistent way nor does it enable (1) useful extrapolation of the data to other conditions, (2) useful quantitative comparisons between different studies, or (3) physically meaningful kinetic parameters to be obtained. The ultimate result has been confusion regarding the effects of reaction parameters such as atmosphere and temperature and of catalyst properties such as support, promoters, etc., on sintering rates.

Fortunately, a new approach to the analysis of sintering kinetics introduced by Fuentes et al. [19,20], the "General Power Law Expression (GPLE)," provides for the first time the capability of analyzing available kinetic data in a consistent, unifying fashion in such a way that quantitative comparisons regarding effects of reaction conditions and catalyst properties are now possible. Moreover, a recent Catalytica study [16] and two recently published reviews [17,18] provide a GPLE analysis of most of the previously published sintering kinetic data.

The purpose of this review is to summarize briefly from the new GPLE perspective *what has been learned from experimental studies of supported metal catalysts* regarding the kinetics of sintering. Companion reviews [17,18] provide more comprehensive analyses of kinetic data and mechanistic information obtained from model supported catalysts [17] commercially-relevant real supported metal catalysts [18]. The discussion in this paper focuses on the effects of atmosphere, temperature and catalyst properties on the kinetics of sintering of the letter group of catalysts.

2. GPLE ANALYSIS OF AVAILABLE KINETIC DATA FOR SINTERING OF SUPPORTED METALS

From previous experimental studies of sintering [2,9,11,12] it is evident that sintering and redispersion are strong functions of temperature, time, atmosphere, and support. Sintering/redispersion rates are also significantly affected by choice of metal and/or promoter, metal loading, and catalyst preparation. The discussion below of previous work will focus on how sintering rates are affected by these variables.

It should also be emphasized that interpretation, comparison, and correlation of previous experimental studies of sintering and redispersion involving supported metals is complicated by the following limitations: (1) relatively few of the previous studies were systematic, i.e. provided statistical data sets carefully defining effects of the important variables, (2) different experimental methods yielding different measures of average crystallite diameter and crystallite size distribution were used, (3) there may have been serious problems in the measurement of dispersion by chemisorption, XRD and TEM in a number of the studies because workers didn't understand the limitations of their technique, (4) it was assumed in most previous studies that particles were distributed uniformly through the catalyst, when in practice the metals may have been distributed in clusters such that local metal concentrations might have been as much as a factor of 10 higher than the mean [21], (5) the support material as well as the metal may have undergone thermally-induced changes, (6) the purity, surface area and pore structure of the support material may not have been specified, and (7) the state of the metal (whether metal, metal oxide, or salt) was not determined in many of the studies.

2.1. Correlation of sintering rate data through rate equations

2.1.1. The simple power law expression (SPLE) and its limitations

Sintering rates have been historically correlated by an empirical rate equation involving either surface area S or dispersion D in a simple power law expression (PLE) of the form:

$$-d(D/D_o)/dt = k_s(D/D_o)^n \qquad (1)$$

where k_s is the sintering rate constant, D_o the initial dispersion, and n is the sintering order, which for typical catalyst systems may vary from 3 to 15 [2]. Unfortunately, this simple rate expression is very limited in its ability to represent experimental data; indeed it is found that sintering orders vary as a function of time, temperature and atmosphere for the same catalyst system. For example, plots of $\log(D_o/D)$ versus $\log(t)$ for sintering of Ni/silica catalysts in nitrogen and hydrogen atmospheres (e.g., Fig. 1) illustrate how the slope n varies with time and temperature from 4 to 15 for a given catalyst and atmosphere [22,23]. Rate constants and activation energies based on Equation 1 are also a function of the reaction order [2,19]. Thus, it is not possible to quantitatively compare kinetic parameters from this rate expression because they are a function of time for the same catalyst even at the same temperature and functions of time and temperature for the same catalyst at different temperatures; comparison of data for different catalysts at the same conditions may be invalid since the data are typically fitted by different sintering orders.

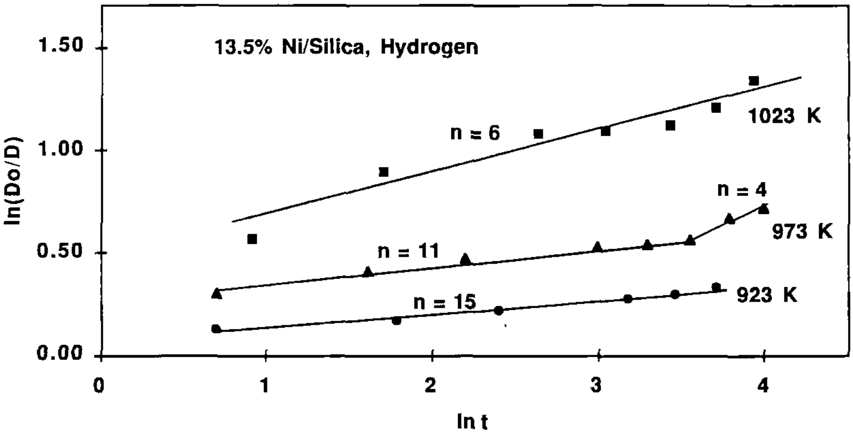

Figure 1. Plot of ln (D_o/D) vs ln t for 13.5% Ni/SiO_2 during sintering in H_2 [23].

2.1.2. The general power law expression (GPLE) and its application to available data: first and second order kinetic parameters

A promising solution to the dilemma discussed above is the application of the general power law expression (GPLE) proposed by Fuentes [19,20],

$$-d(D/D_o)/dt = k_s(D/D_o-D_{eq}/D_o)^m \qquad (2)$$

which adds a term $-D_{eq}/D_o$ to account for the observed asymptotic approach of the typical dispersion versus time curve to a limiting dispersion D_{eq} at infinite time. The introduction of this term is physically meaningful since values of dispersion and metal particle size are generally observed to approach a limiting value with time [24,25]. The GPLE (Eqn. 2) also