Proceedings of the Third International

CONGRESS ON CATALYSIS

Amsterdam 20-25 July 1964

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PREFACE

The Third International Congress on Catalysis was held in Amsterdam, The Netherlands, from 20th to 25th July 1964. Sponsored by the International Union of Pure and Applied Chemistry, it was organized by the Royal Netherlands Chemical Society. The Organising Committee consisted of: Prof. Dr. J. H. De Boer (President), Prof. Dr. G. C. A. Schuit (Vice-President), Dr. D. M. Brouwer (Secretary), Ir. P. W. Pfeiffer (Treasurer), Dr. Ir. J. W. E. Coenen, Dr. O. Drexler, Prof. Dr. G. J. Hoijtink, Miss C. E. Huisken (Congress Bureau of the City of Amsterdam), A. I. De Jong, Prof. Dr. W. M. H. Sachtler, Prof. Ir. H. W. Slotboom, Dr. Ir. G. S. Van der Vlies, Prof. Dr. Ir. J. C. Vlugter and P. Zwietering.

Approximately 800 scientists from 31 countries took part in the Congress while 225 people were registered as accompanying members.

The scope of the Congress had been limited to the subject "*The Mechanism of Heterogeneous Catalysis*", the main topics being *Molecular description of the catalytic reaction,* and *Selectivity in heterogeneous catalysis*. Ninety-eight contributions had been accepted for presentation, preprints of which had been sent to all participants six weeks before the Congress. These contributions were presented and discussed in a series of sessions, two simultaneous sessions being held at a time. Five minutes were reserved for introducing each contribution and fifteen minutes for discussing it. Generally, the discussions were lively and yielded much up-to-date information and new views.

In addition six invited speakers lectured to the whole assembly on subjects related to the main theme of the Congress. These lectures were excellently presented by Prof. Dr. G. K. Boreskov (Novosibirsk), Dr. G. Ehrlich (Schenectady, N.Y.), Prof. Dr. J. Halpern (Chicago), Dr. H. Hoog (The Hague), Prof. Dr. R. S. Nyholm (London) and Prof. Dr. V. V. Voevodsky (Novosibirsk) and formed a most stimulating part of the Congress.

The social side of the Congress was not neglected and a series of well attended and lively functions helped to promote contact between the participants. These functions included an informal get-together in the evening before the beginning of the Congress, a reception in the Rijksmuseum by the Dutch Government and the City of Amsterdam, a boat-trip through the harbours and canals of Amsterdam offered by the City of Amsterdam, and a cocktail-party on the evening of the last full day of the Congress.

A special programme of visits to various parts of the country was organised for the accompanying members and an afternoon was reserved for general excursions for all participants.

At a business meeting attended by about 200 participants it was decided to hold the Fourth International Congress on Catalysis in the Soviet Union in 1968.

Acknowledgements

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The North-Holland Publishing Company (Amsterdam) accepted to publish the Proceedings of the Congress. The Organizing Committee wishes to express their appreciation for the pleasant collaboration between Publisher and Committee during the preparation of the preprints as well as of the Proceedings. The products of this collaboration are herewith presented to all scientists interested in catalysis.

J. H. De Boer
President Organizing Committee
Third International Congress on Catalysis

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INTRODUCTION

J. H. DE BOER
Technological University, Delft, The Netherlands

"It is already many thousands of years ago that man, using his powers of observation and analysis, mastered some catalytic processes." This important statement is a free translation of the first sentence of a delightful little book [1] written by my predecessor in my present capacity.

At the end of his booklet Prettre concludes that catalysis has at last acquired a place of primary importance in science and in industry. The Second International Congress on Catalysis, which took place in Paris in 1960 and which was presided by Prettre, was a demonstration of these facts. A second congress, obviously succeeds a first one, but it is also obvious that the first one has not been announced with that number. With it we mean the International Congress on Catalysis, organized by our American colleagues in Philadelphia in 1956. As Dr. Farkas states in the Proceedings of that Congress [2], the original idea was conceived by the Catalysis Club of Philadelphia (Penn.) and although several international Congresses, Discussions or Symposia on Catalysis had been held in Europe before, it was the first one in the United States of America. Even more important, however, was the fact that during that Congress, since called The First International Congress on Catalysis, the decision was taken to hold a second one in 1960, and that during the second one it was decided again to hold a third one, this time in the Netherlands. The present Netherlands Organization Committee decided to organize it in Amsterdam.

During this week, to be precise on Wednesday evening, 22nd July, during the so-called "business meeting" we plan to discuss the possibility of a fourth one. The Catalysis Club of Metropolitan New York has already notified us of their intention to invite us to ask them to organize the Fourth International Congress on Catalysis in their metropolis. More offers may come forward before or during that decisive evening, and I shall be glad to receive them.

During that same Business meeting the question whether or not a permanent international body is needed for the organization of future Congresses on Catalysis will be discussed. Every active participant in our meeting has been given a copy of a draft constitution which will be discussed if and when the decision is taken to form an international organisation.

The Third International Congress on Catalysis has, at least, one important thing in common with its two predecessing Congresses. It has been made possible by generous donations. The Netherlands Government, the

City of Amsterdam, the International Union of Pure and Applied Chemistry and 18 important industries in this country, the names of which are printed on page 3 of the programme, enabled the Committee to perform their task. I want, also from this place, to express my great appreciation for their generous support. Five large industries have given an extra large financial support; they are: Shell Nederland N.V. (comprising the "Bataafse Internationale Petroleum Maatschappij" and the "Bataafse Internationale Chemie Maatschappij), Unilever N.V. (comprising Van den Bergh and Jurgens N.V., Levers Zeep Maatschappij N.V., Unox N.V. and Iglo N.V.), Staatsmijnen in Limburg, Koninklijke Zout - Ketjen N.V. and Philips' Gloeilampenfabrieken N.V.

I want also to thank the directors of three large research laboratories, who materially supported us by allowing members of their staffs to dedicate much time to the work of the Organizing Committee; these laboratories are those of Shell Research N.V. in Amsterdam, Staatsmijnen in Limburg in Geleen and Ketjen in Amsterdam. Our thanks go also to the Congress-Bureau of the City of Amsterdam for their advise and actual help and to the North-Holland Publishing Company, who succeeded in preparing the preprints well in time to distribute them to all parts of the world several weeks before the Congress. We thank Dr. Ciapetta for the work, which he undertook to distribute the preprints, which we sent to him in bulk, among the U.S. participants. I observed that they were in the hands of some participants when I was over there in the first half of June.

The growth in size from the First to the Second International Congress on Catalysis may be well demonstrated by comparing the volume of the Proceedings of the Philadelphia Congress, which consists of 847 pages, with the Proceedings of the Paris meeting, which is bound in 2 volumes, comprising 1397 pages [3]. The Organizing Committee of the present Congress knew that the Proceedings of the First Congress contain some papers, which have not been read. I also knew, even from experience, that the Organizing Committee of the Second Congress had already tried to restrict the size by not accepting some papers. The present Committee, therefore, decided to limit the scope of the Congress and to exclude – this time – homogeneous catalysis and biocatalysis and to restrict the Third Congress to two topics falling under the heading of the theme: The Mechanism of Heterogeneous Catalysis. The two topics, as set out in our second circular, are:

1. Molecular description of the catalytic reaction and its intermediate states.
2. Selectivity in heterogeneous catalysis.

Despite these serious restrictions 130 papers were sent in. The Paper Selection Committee had a most difficult task. They arrived at the conclusion that 32 papers had to be refused admission, because they did not comply with the rules which the Committee wanted to maintain. Some of these not accepted papers have found their way already to appropriate journals; in my function of one of the two editors of Journal of Catalysis I have admitted already some for publication. In order not to give you a wrong idea, I am not a member of the Paper Selection Committee and I have, on purpose, not associated myself with their difficult business. Glancing at the titles

and looking in the preprints I get the impression that the Paper Selection Committee have made a good job of their difficult task.

It is interesting to observe that the number of authors per paper increases in the course of time. This is, perhaps, a result of the increasing importance of team work in research laboratories. I like to illustrate this statement with a few figures, which I shall give in the form of two tables.

Table 1

Congress	Number of papers	Total number of authors	Authors/papers
I (1956)	81	157	1.94
II (1960)	144	325	2.26
III (1964)	98	250	2.55

Table 2

Percentages of papers, written by:	Ist Congress 1956 (%)	IInd Congress 1960 (%)	IIIrd Congress 1964 (%)	Trend
1 author	31	26	18	Decrease
2 authors	47	39	35	Decrease
3 authors	20	22	28	Increase
4 or more authors	2	13	19	Increase
	100	100	100	

Despite the restrictions the Organizing Committee regret that it has not been possible to avoid parallel sessions. We have tried to cover some of the interesting subjects which were excluded from the Congress discussion papers by arranging for general lectures and we are very thankful that the six speakers of these general lectures have been willing to assist us in every respect.

Last year the Italian Government drew the attention to the fact that in 1564, hence now 400 years ago, Michel Angelo died and that Galileo was born in the same year. They asked to consider the possibility to draw the attention to these facts at proper occasions. I think this is a proper occasion. Arts and Sciences are far more related than many will admit. Michel Angelo the sculptor, the painter, the architect taught us how to see things, to form for ourselves a picture of our observations. Galileo promoted dynamical studies in Physics. Both together remind us at the two topics of our present Congress. Our first topic asks us to form for ourselves a picture, the second draws our attention to the dynamical character of our studies. They complement each other, the first comes first, the second may then follow. In this context it is nearly significant that Galileo was born on the 15th of February 1564, two days before Michel Angelo died on the 17th of the same month. It is as if Providence would remind us of a continuity between forming a picture and, having done this, studying the changes.

We all know how dangerous it may be to deduce the mechanism of a

catalytic reaction, hence the picture, from kinetic observations. On the other hand, kinetic observations may give a useful check on the picture which we have made.

Recently we have had an interesting case in my Delft laboratory, studying the dehydration reaction of ethylalcohol on alumina. For the rate of the reaction:

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O ,$$

as a function of the alcohol pressure at a constant temperature (305°C), we obtained a curve as in fig. 1; denoting with low pressures, a second order reaction, which changes into a first order one at higher pressures. Without

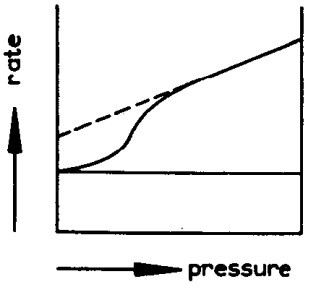

Fig. 1.

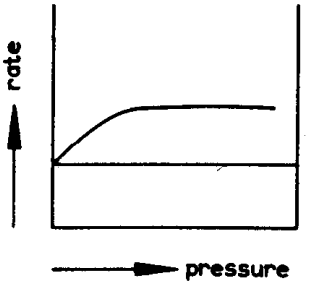

Fig. 2.

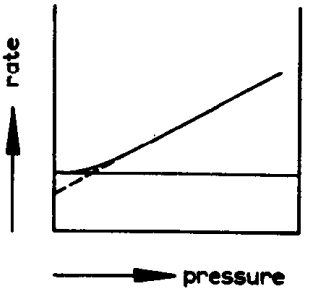

Fig. 3.

additional information one might conclude that, with higher pressures, a pseudo first order reaction is similated by a too slow diffusion of alcohol towards the catalyst. Simultaneously, however, another reaction takes place on the same catalyst at this temperature:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O ,$$

the dependance on pressure of which is given by fig. 2. This reaction starting as one of first order becomes a zero order reaction at the same pressure as the ether-formation becomes first order. Apparently, at this pressure and at 305°C, the alcohol molecules form a completely covered unimolecular layer on the active spots of the alumina. We may conclude that the ether formation proceeds – partially – via an Eley-Rideal mechanism, one alcohol molecule reacting from the gaseous or van der Waals' adsorbed state with a chemisorbed alcohol molecule. Partially, because, if entirely, the curve for the ether formation should be as in fig. 3. The experimental curve can be understood by a combination of an Eley-Rideal mechanism and a Langmuir-Hinshelwood mechanism, as given by fig. 4 *. The experimental curves [4] for two sorts of Al_2O_3, namely γ-Al_2O_3 and η-Al_2O_3 may be given in figs. 5 and 6. The pre-treatment of our alumina samples had been such that, anyhow, diffusion difficulties could hardly have been expected.

With respect to diffusion problems the study of the width, and the

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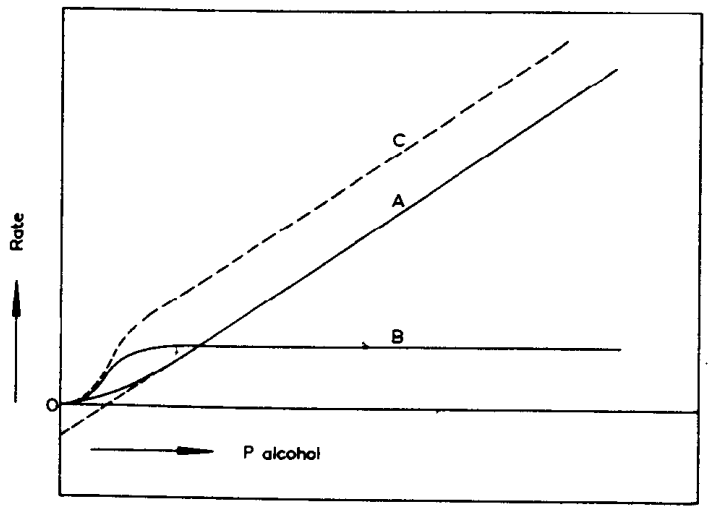

Fig. 4. Curve A (Eley-Rideal mechanism) and curve B (Hinshelwood-Langmuir mechanism) together yield curve C.

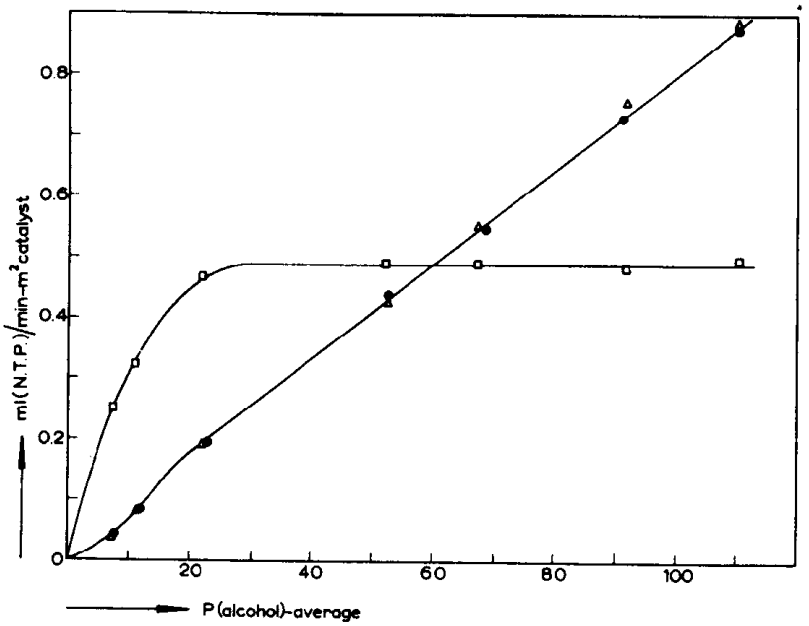

Fig. 5. Production of ethylene (□) and of ether (● and Δ) on γ-Al_2O_3.

shape, of the capillaries in catalysts may be recommended. It is, at present, customary to measure the specific surface areas of the catalysts which are used. The BET surface areas are often published. I have, however, already noted that about 20% of the papers in our present Congress do not give the BET surfaces, although it might have been better to have done so. Details about pore widths and shapes, however, are far less frequently