

# **8th International Congress on Catalysis**

**Proceedings**

**Vol. 1**



# 8th International Congress on Catalysis

Volume I: Plenary Lectures



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**The lectures announced in the programme bear the following relationship to the manuscripts in the Proceedings in the following manner.**

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<p>Plenary Lecture W. M. Sachtler (see Pr. page 30 Vol. I-151)</p> <p>Catalysis for reactions with synthesis gas (see Pr. page 30 Vol. II-3-82)</p>	<p>Dynamics of Catalytic reactions (see Pr. page 31 Vol. III-265-276, 311-332, 347-358, 441-452)</p> <p>Active phase-support interactions (see Pr. page 31 Vol. V-147-194)</p>	<p>Structure selectivity/ activity correlations (see Pr. page 48 + 49 Vol. IV-381-656)</p> <p>Studies on the working catalyst (see Pr. page 50 Vol. II-533, 569-601, 613-705)</p>

## Preface

The 8th International Congress on Catalysis differs in several respects from its predecessors. Because of the overwhelming response of the catalysis community to the call for papers, the organizing committee accepted about twice as many contributions as were presented at previous congresses; still, more than half of the submitted abstracts had to be declined. To maintain the usual format of only two parallel sessions, the majority of papers will be presented as posters. The proceedings have been published in bound form prior to the Congress. It is hoped that the early publication will stimulate discussion while saving the cost of separate preprints. The discussion contributions, together with a summary and evaluation to be written by Professor M. Boudart, will be published as a separate volume after the Congress.

The Berlin Congress coincides with several important anniversaries marking the history of German catalysis. Seventy five years ago Ostwald was awarded the Nobel prize for his contributions to catalysis and fifty years ago Polanyi and Horiuti published their mechanism for ethylene hydrogenation based on work performed in Berlin. The 100th birthday of Arnold Eucken and the 75th anniversary of the first realization of catalytic ammonia synthesis by Fritz Haber — who died fifty years ago — will be commemorated in special contributions by Professor Schwab and Professor Timm.

The organizing committee was immeasurably assisted in its task by the staff of the Deutsche Gesellschaft für Chemisches Apparatewesen (DECHEMA), who accepted the responsibility for a large part of the organization. We also gratefully acknowledge the generous support provided by the Senate of Berlin and the Federal Minister of Science and Technology, as well as by the following Sponsors:

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It is our sincere wish that participants from all over the world enjoy a stimulating and fruitful conference and return home with a lasting impression of this unique city.

G. Ertl  
Chairman

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## **HISTORICAL LECTURES**





## EUCKEN's Work on Catalysis

G.-M. Schwab

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On the occasion of the 8. International Congress on Catalysis it is a duty to remember an outstanding catalytic chemist, born exactly one hundred years ago tomorrow, namely 3rd July 1884: Arnold Thomas Eucken. He left us 34 years ago, 16th June 1950. Since his hundredth birthday coincides with the present Congress, we should remember his activities in the field of catalysis today, especially because the world knows Eucken mainly by his achievements in thermodynamics, rather than in catalysis. Most of his work on adsorption and catalysis was done before, during, and after the World Wars and remained unknown in many parts of the world. However, it is notable that many of Eucken's ideas are still valid in catalysis today.

In 1914 Eucken first published his "Thoughts on the theory of adsorption". In this remarkable article he derived the basic laws of adsorption before Polanyi, Freundlich, and Langmuir, including, for example, the isobar, for which he gave examples. Surface roughness and capillary condensation were also taken into account.

In his next article in this field the nature of the adsorptive forces was derived from experiments (1922). By then, Langmuir's results were already available. However, Eucken's views were different: the linear rise of the isotherm was not explained by the impact equation, but by a kind of sedimentation equilibrium. For this, the adsorption potential must be assumed to be independent of temperature, and this was confirmed.

After a long period, the first calorimetric investigation of physisorption and chemisorption was undertaken in 1939. The energy profiles, generally known today as "Lennard-Jones potentials" were being used by him as well as a special microcalorimeter. His results for hydrogen on nickel were 3.3 kJ/mol for physisorption (at 20 K) and ca. 84 kJ/mol for chemisorption ( $> 90$  K). A tunnel effect for the transition between the two states could be excluded.

In treating the dehydration of alcohols on alumina in 1944, Eucken wrote of "Hydrogen exchange catalysis", now described as a concerted reaction scheme. Here for the first time the "Franck-Condon principle" was introduced into reaction kinetics. All its consequences (activation by water and by oxygen atoms) were confirmed experimentally. In 1947 these results were corroborated and extended to the mechanism of dehydrogenation of alcohols on oxide catalysts.

In 1949 the new principle, now called the "reaction kinetic principle of least motion", was applied to new examples, namely, the isomerization of butenes and the dehydration of propanol and other alcohols.

Parallel to these investigations, the industrially important hydrogenation of unsaturated hydrocarbons was studied as another model catalytic reaction. Polycrystalline Ni powder was considered to be representative of Ni catalysts, and the chemisorption of hydrogen in the range 0 to 270 - 470 K was studied by calorimetry, hysteresis effects were observed on the adsorption isobars which could be attributed to rate limitations. The results of adsorption rate measurements and their interpretation: the decrease of the heat of adsorption with increasing coverage and the transitions between different states of the chemisorption hydrogen correspond closely to modern viewpoints. Eucken generally emphasized different chemisorbed states on surfaces regarded as uniform, instead of making use of the concept of different active centers, according to Taylor. However, from subsequent catalytic hydrogenation measurements for cyclohexene and ethylene, Eucken drew conclusions that are no longer accepted, today. This holds particularly for his concept that hydrogen atom pairs at the surface are the active species which react with the hydrocarbon molecules from the gas phase and that hydrogen atoms chemisorbed separately act as inhibitors of the reaction.

In the same year (1949) a general treatise on contact catalysis appeared. In the introduction, the parallels between catalytic and chain reactions were emphasized. The action of hydrogen atoms as chain carriers was illustrated, especially for isomerizations. Dehydration and dehydrogenation were symbolized by models, and, the former ideas in the sense of the Franck-Condon model were repeated and completed for hydrogenation.

In 1950 extended measurements of alcohol decomposition on a large number of different oxides were evaluated with regard to correlations between the ratio of dehydration to dehydrogenation and characteristics of the oxides, such as lattice structure, ionic radii, and ionization energies. A contribution to the Faraday Discussions on "Heterogeneous Catalysis" in that year dealt with the general question of active centers. Eucken addressed the question as to whether a surface possesses different sites or the adsorbed molecules different states. It is remarkable that even when he could not avoid the idea of active centers, he still emphasized the existence of different states.

The last paper on catalysis written by Eucken appeared posthumously in 1951. It describes the changes of a platinum electrode resulting from the transition of hydrogen ions to adsorbed atoms, measured by the change of polarisation capacity.

With this investigation, a return to his early electrochemical studies, Eucken's work on catalysis ended abruptly. It led him through the whole field of heterogeneous catalysis and adsorption, where he dealt with many of the most important areas. If he did not always arrive at the final solution, this may be attributed to the sudden end of his life of untiring research activity. We bow our heads before this great man of catalysis.

List of Eucken's publications on adsorption and catalysis

- 1914 On the Theory of Adsorption.- Verh.d.D.Phys.Ges. 16(1914) 345
- 1922 On the Theory of Adsorption Processes - Z.Elektrochem.28 (1922) 6
- 1944 The Interpretation of Heterogeneous Dehydration Catalysis by the Exchange of Hydrogen Atoms. - Naturwiss.32 (1944) 161 (with E.Wicke)
- 1947 On Hydrogen Exchange Catalysis on Oxidic Contacts.- Z. Naturforsch. 2a (1947) 163 (with E.Wicke)  
A Model for the Inhibited Chemical Adsorption of Hydroxylic Compounds on  $\gamma$ - $\text{Al}_2\text{O}_3$ . - Naturwiss.34 (1947) 374  
Exchange Contact Catalysis.- Forsch. u. Fortschr.21/23 (1947) 79
- 1949 The Hydrogenation of Unsaturated Hydrocarbons on Nickel Contacts:  
I. The adsorption of Hydrogen on Nickel.- Z. Elektrochem. 53 (1949) 285  
II.Reaction Kinetic Investigations.- Z. Elektrochem.54 (1950) 108  
Investigations on Contact Catalysis.-Naturwiss. 36 (1949) 48,74
- 1950 To the Knowledge of the Catalytic Dehydration and Dehydrogenation of Alcohols on Oxides.- Z.phys.Chem. 196 (1950) 40 (with K. Heuer)  
On the Existence of Active Centers in Chemical Adsorption and Contact Catalysis.- Disc.Faraday Soc.8 (1950) 128
- 1951 Adsorption of Hydrogen on Platinum According to Measurements of Polarisation Capacity.- Z. Elektrochem.55 (1951) 114 (with B. Weblus)



## The ammonia synthesis and heterogeneous catalysis

### A historical review

B. Timm, former Chairman of the Board of BASF, Ludwigshafen

As every chemist knows, the synthesis of ammonia, in which the nitrogen of the air is hydrogenated at high pressure on a heterogeneous catalyst, marked the beginning of a new era of industrial catalysis (1). The synthesis of methanol followed only a few years later, and high pressure reaction techniques in the presence of a heterogeneous catalyst subsequently became standard practice in the field of organic chemistry. Nowadays, this technology is a valuable tool for the chemist and many key products are obtained in this way. In order to carry out research on the synthesis of ammonia it was necessary to develop and construct apparatus which was completely new in its conception. It was for this purpose that the Ammonia Laboratory was founded at BASF in Ludwigshafen, and for many years this was the largest industrial chemical research facility in the world.

In 1784 C.L. Berthollet was able to demonstrate that ammonia is composed of the elements nitrogen and hydrogen (2). The chemists of the time then immediately attempted to confirm this result by synthesizing ammonia from the elements. They found themselves, however, confronted by seemingly insurmountable obstacles.

Despite countless efforts, another 125 years were to pass before Fritz Haber (fig. 1) succeeded in preparing ammonia for the first time on 2nd July 1909



Fig. 1 Fritz Haber (1868 - 1934), winner of the 1919 Nobel Prize, laid the foundations for the technical synthesis of ammonia

- exactly 75 years ago - using his high-pressure apparatus (3). The reason for the previous failures was simply that at the time of the earlier experiments the laws of mass action and chemical equilibrium were still unknown. As a result of advances in physical chemistry, and thanks to studies on the equilibrium of ammonia at various temperatures and over a wide range of pressures, it became clear that the synthesis of ammonia should, indeed, be possible. The synthesis would, however, require reaction conditions which had never been employed up to that time, and would necessitate the use of equipment which had yet to be developed. Prominent chemists of the period, including such names as Nernst, Ostwald and Haber, devoted intensive effort to the problem, but up until the end of 1907 they continued to encounter setbacks due to incorrect or questionable interpretation of their experimental results.

It was, however, now clear why previous experiments had failed. It was recognized that for thermodynamic reasons (fig. 2), ammonia could be formed at

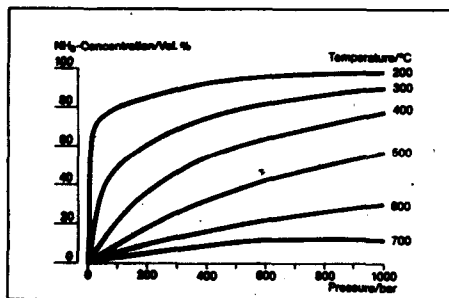


Fig. 2 The equilibrium concentration of ammonia  

$$\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$$
  
 as a function of pressure and temperature.

normal pressure only at relatively low temperatures, i. e. below 300 °C, and then only to an extent of a few percent (4). There was, however, no known catalyst which was capable of accelerating the reaction under these conditions. On the other hand, if the pressure were raised to approximately 75 bar

and the temperature to over 600 °C the yield of ammonia would be drastically reduced due to the decomposition of the ammonia molecule under these conditions. A number of scientists of the day even believed that there were insurmountable obstacles which utterly precluded the formation of ammonia from the elements. It was just at this point that Fritz Haber achieved a breakthrough and found the way to overcome the prejudices which blocked the thinking of his colleagues. He realised that it would be necessary to work at much higher pressures than hitherto. It was this idea which provided the basis for the construction of an experimental unit for the continuous production of ammonia. Haber was fortunate enough to have a highly skilled assistant for his experimental work, Robert le Rossignol. Despite his French-sounding name, the latter was an Englishman, who later taught physical chemistry at Harrow. Figure 3 shows the experimental set-up which was built in Haber's institute in Karlsruhe. It was with this apparatus that 90 g of ammonia per hour were produced for the first time on 2nd July 1909.

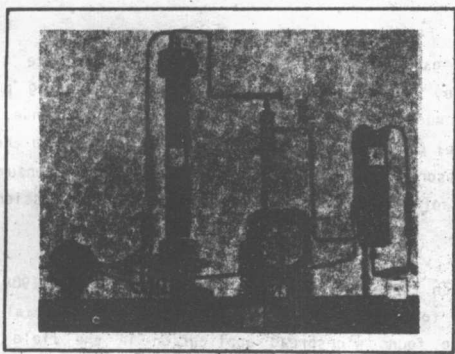


Fig. 3 Haber's experimental apparatus for the synthesis of ammonia (1909).  
(taken from (3))

The quantity of ammonia formed by a single pass through the reactor was, however, far too small for the purposes of industrial-scale production. It was then that Haber had the brilliant idea of operating the reactor as a closed circuit by recycling the gas-mixture over the catalyst, as shown in Figure 4.



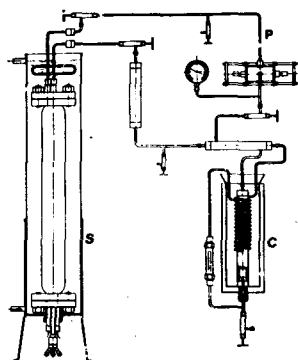


Fig. 4 Diagram of the recycle apparatus for the synthesis of ammonia (Haber 1909). (taken from (5)).

In this case, the gas mixture is recycled at high pressure through the reactor S containing the catalyst by means of a circulating pump P. The ammonia which is produced is removed from the system, for instance, by cooling the separating vessel C. Fresh synthesis gas is then pumped into the system by means of a compressor in order to replace the quantity consumed by the reaction. This mode of operation has the advantage that compression energy is saved.

This procedure, which is described in the patent DRP 235 421 (1908), provided the real foundation for the synthesis of ammonia on an industrial scale. The same principle also found widespread application in the field of organic chemistry, where it was employed for numerous reactions carried out under high pressure.

Haber's idea of operating in a closed circuit and recycling the gas mixture meant that he abandoned the prevailing static view of chemical science and adopted a more dynamic approach by considering the kinetics of the reaction. Parallel to the concept of thermodynamic equilibrium he introduced another principle of comparable importance, namely the concept of reaction rate. Instead of reaction yield he considered the space-time yield. In this way it became apparent that the problem amounted to finding a suitable catalyst.