

8th International Congress on Catalysis

Proceedings

Vol. 6



8th International Congress on Catalysis

Volume VI: Discussion-remarks



Weinheim
Deerfield Beach, Florida
Basel



Responsible for the contents: The Authors

(Their ready-for-copy manuscripts have been printed without corrections)

All rights reserved

© 1985 by DECHEMA, Deutsche Gesellschaft für chemisches Apparatewesen e.V.
Frankfurt am Main

Printed: Schön & Wetzel GmbH, Frankfurt am Main

ISBN 3-527-26230-X (Weinheim, Basel)

ISBN 0-89573-374-9 (Deerfield Beach)

A POSTSCRIPT

M. Boudart

Stanford University

USA

Some observers inside and outside catalysis have expressed the view that the field is mature. Thus, they say, exciting discoveries and innovations are not as likely to happen in pure or applied catalysis, as in molecular biology or biotechnology. The program of the 8th International Congress on Catalysis, held in July 1984 in Berlin, belies such a pessimistic assessment, both qualitatively and quantitatively.

From the viewpoint of quantity, the organizing committee faced some difficult decisions. The number of submitted abstracts was four times the number of papers accepted at previous congresses. One way out of this situation would have been to restrict the scope of papers by applying a strict definition of the subject matter such as that of Jack Halpern (the emphasis is his own): "Catalysis, by definition and significance, is wholly a kinetic phenomenon. However interesting may be the study of the physical and chemical properties of species involved in catalytic systems, it is only to the degree that the results of such studies can be related to the rates of catalytic processes they are relevant to catalysis." (1).

This definition is quite correct and its spirit remains in agreement with that of the first modern book on the subject (2). Yet catalysis is an applied subject that finds its inspiration in many areas of science and

the purpose of a Catalysis Congress is to bring together as many participants as possible from all related disciplines.

In a Solomon-like compromise, the organizers of the Berlin Congress accepted only half of the submitted abstracts. Still the number of contributions presented in Berlin was twice as large as that of other congresses. To accommodate this bounty, the organizers introduced an astute innovation, namely to accept 72 papers for oral presentations and 199 for poster presentations. In this way, it was possible to hold only two parallel sessions while the poster presentations were taking place on the side. Yet, the poster sessions were in no way to be considered as the *salon des refusés*. Some of the best communications were presented in poster sessions. Besides, all communications plus the plenary lectures were published in 5 hard bound volumes available before the meetings. In a concession to economic realities, these volumes consisting of Spartan photo-ready copy of excellent or very poor quality, also represent the final publication of the Congress proceedings, together with the 6th volume for the discussion of the oral presentations. These two new features of the International Congress on Catalysis, namely a large fraction of communications to be accepted for poster sessions and final pre-publication of all communications, will certainly be affecting the style of congresses to come. Organizing committees will grapple with such issues but if they are as lucky as the Berlin Congress committee in their pick of plenary lectures, they will have won half of the battle. Indeed, plenary lectures are the mechanism for gathering together all attendees to listen to leaders in their respective fields give their perspective on new directions of research in catalysis.

The choice of the five plenary lecturers was indeed exceptional: all of them were excellent speakers with a provocative message. Their written lectures will be cited for a long time. They represented five frontier topics: New Instrumentation for New Catalytic Materials (J.M. Thomas), Strategies for Synthesis of New Organometallic Catalysts (L.M. Lehn), Solid State Chemistry in Catalyst Optimization (J. Haber), Structural Chemistry in Molecular Reaction Mechanism (G.A. Somorjai), and Modern Process Research for Catalyst Improvement (W.M.H. Sachtler).

I shall now attempt to review these five topics which were illustrated by many papers presented in the oral communications and in the poster sessions. The relation between the plenary lectures and the communications is spelled out in a clever front page in the first volume of the proceedings. This useful device dispenses me from referring to any of the 271 communications to the Congress. To refer to all of them is impossible. To refer to some of them would be invidious.

The lecture by J.M. Thomas is an eloquent testimony to the continuing improvement in our ability to characterize catalytic materials with structural details revealed by improved instruments. The main examples chosen deal with zeolites as examined by high resolution electron microscopy and multi-nuclei solid state nuclear magnetic resonance. These powerful tools complemented by absorption and scattering of X-rays from a synchrotron source are just starting to do for catalytic materials what electron spectroscopic techniques have done for single crystal surfaces over the past 20 years. An added advantage of these X-ray techniques, as pointed out by Thomas, is that they lend themselves to in situ studies of the working catalyst (3). History of heterogeneous catalysis shows that the

subject has advanced in discrete leaps each time a new tool has appeared to characterize old and new catalytic materials. The lecture of Thomas was particularly well timed to give a survey of two new important tools.

But how does one invent new catalytic materials? A strategy is outlined by J.-M. Lehn in a paper dealing in part with catalytic photochemical splitting of water, a dream already formulated by Jules Verne as Lehn pointed out at the end of his lecture in Berlin. The goal has not been reached but the task is clear: to discover catalytic reactions for activation of water as well as light absorbing materials that undergo photoinduced transfer processes. Various types of catalysts have been synthesized: photocatalysts, electron transfer catalysts, and reaction catalysts which may be homogeneous or heterogeneous. Model systems have been built to carry out the separate photogeneration of H_2 or O_2 with consumption of a sacrificial electron donor or acceptor. The ultimate goal is to produce H_2 or O_2 simultaneously. Lehn also discusses artificial photosynthesis involving carbon dioxide. He concludes by pointing out how artificial photosynthesis may further contribute to the development of chemical catalysis. The catalytic systems include not only organometallic complexes but microheterogeneous systems of increasing sophistication (4). Thus the type of science reviewed by Lehn is typically peripheral to chemical catalysis but of a kind that is likely to influence greatly chemical catalysis itself, because of the methodology used in the rational development of new catalytic systems.

By system, I mean here a molecular entity of a certain complexity. Such systems are found in the solid structures used in catalytic selective oxygenation processes and studied over the years in the laboratory of

J. Haber from the viewpoint of dynamic solid state chemistry. This is the viewpoint stressed by Haber in his Berlin lecture. The dynamics of the solid surface includes a subsurface layer of defect oxide which participates in the activation of dioxygen at the surface and the insertion of oxygen into the substrate. According to Haber, the lesson is that, for such catalytic systems, when the steady-state conditions of the reaction are changed, the structure and composition of the surface may also change, with a corresponding change in activity and selectivity. This dynamic behavior of the catalytic surface region of transition metal oxides finds its roots in the seminal work of Wagner and Hauffe dealing for the first time with the role of the defect solid state in catalysis (5).

Unfortunately, overenthusiasm about the ensuing semiconductor theory of catalysis culminating about 25 years ago, has temporarily obscured the usefulness of these concepts. It is very encouraging to find them rise again phoenix-like in the work of the Haber group. The concepts clearly have application beyond selective catalytic oxygenation.

The next plenary lecture by G.A. Somorjai, gives us an idea of the progress accomplished in our understanding of catalysis at metal surfaces as a result of the application of surface science techniques to large atomically clean single crystal surfaces. Even though these surfaces are not always as well-defined or atomically clean as commonly believed, they are much better characterized than the surfaces of metallic oxides covered by the lecture of Haber. To the extent that they are well characterized, metallic catalytic surfaces are understood at a molecular level in a much more quantitative way than any other kind of solid catalyst with the exception of zeolites. Thanks to the advent in Somorjai's laboratory of

rate measurements at normal pressures on a single crystal followed by an autopsy at very low pressures with the help of electron spectroscopic methods, a list of rate measurements has been growing over the past few years, with excellent agreement between results obtained on macroscopic single crystals and the very small supported crystals used in industrial catalysis (6). So much so that it is now possible to state that for metallic catalysts, work on large single crystals provides the standards by which work on industrial catalysts can be assessed (7). Measurements of catalytic rates on single crystals at normal pressures are now so widespread (8) that the "impact of surface science on catalysis", the umbrella title of the communications dealing with work related to the lecture of Somorjai, may be considered in my opinion as the most important positive impact on heterogeneous catalysis for the past ten years. And the future, as outlined with great enthusiasm by Somorjai, looks very bright indeed.

The last plenary lecture by W.M.H. Sachtler differs from the others in the sense that it is the only one that deals with the possible improvement through basic research of an existing process, the building up of compounds with more than one carbon atom by reactions between CO and H₂ in synthesis gas. This is a particularly fascinating paper because it presents new results obtained in a program involving work at the Koninklijke Shell Laboratorium in Amsterdam and the University of Leiden. The author presents an intriguing new model of the catalyst surface that is intended to explain a facilitated dissociation of CO. This is certainly an unusual paper among so many that have appeared on the subject since the mid 70's when the topic became fashionable, including a large number of papers on CO-H₂ chemistry presented at the Berlin

Congress. The dust has not settled yet on this major assault on one of the most complex problems in catalytic process chemistry. It may well be that the next major industrial improvement of this family of processes will not come from improved understanding of reaction mechanism but through an astute application of catalytic reaction engineering principles to both catalyst design and reactor design.

In summary, as a result of an excellent selection of plenary lecturers, of using the topics of these lectures as unifying themes of the Congress, of accepting a record number of communications for oral presentations and poster sessions, and of publishing all communications, the organizers of the Berlin Congress did stage a difficult act to follow. The Proceedings of the Congress will remain a permanent record of the vitality of catalysis in the 80's. This vitality should be viewed through the historical perspective provided by B. Timm in his historical review that opened up the Congress. It is an account of the development of ammonia catalysis that took place within an amazingly short time in Germany just prior to the first World War. For those of us who have become accustomed to the formidable arsenal of tools used in contemporary research and development in catalysis, it is sobering to note first that the winning ammonia synthesis catalyst was discovered through a brute force screening process that ultimately involved more than 10,000 tests and more than 4,000 catalysts. The second fact to note is that the original winning catalyst is still with us today essentially unchanged. This is the kind of lore that leads some observers to say that catalysis is a mature field as I remarked at the start. Perhaps, but mere inspection of the Proceedings of the Berlin Congress will reveal the vigor of

this mature field in new instrumentation, materials, mechanisms, and methodology.

REFERENCES

1. Jack Halpern, in "Relationship Between Homogeneous and Heterogeneous Catalysis," B. Imelik *et al.* Eds., CNRS, Paris 1978, p. 28.
2. Georg-Maria Schwab, Catalysis From the Standpoint of Chemical Kinetics," Hugh S. Taylor and R. Spence, Translators, D. Van Nostrand Company, Inc., New York 1937.
3. P. Gallezot, "X-ray Techniques in Catalysis," in Catalysis: Science and Technology, J.R. Anderson and M. Boudart, Eds., Springer, Heidelberg, 1984, Vol. 5, p. 221.
4. M.D. Archer, Chem. in Britain 20, 991 (1984).
5. C. Wagner and K. Hauffe, Z. Elektrochem., 4, 172 (1938).
6. M. Boudart and G. Djéga-Mariadassou, "Kinetics of Heterogeneous Catalytic Reactions", Princeton University Press, Princeton, 1984, p. 157.
7. M. Boudart and D. Löffler, J. Phys. Chem., in press.
8. D.W. Goodman, Acc. Chem. Res., 17, 194 (1984).

CONTENTS

M. Boudart, Stanford, CA/USA	
Postscript	03—010
Catalysis for reaction with synthesis gas see Vol. II	1— 32
Catalysis for upgrading of crude oil see Vol. II	33— 70
Studies on the working catalyst see Vol. II	71— 84
New methods in catalysis research see Vol. III	85— 94
Dynamic of catalytic reactions see Vol. III	95—130
Contributions of catalysis to ensuring the energy requirements see Vol. III	131—159
Catalysis and environmental protection see Vol. III	— —
Impact of surface science on catalysis see Vol. IV	160—184
Structure — selectivity/activity correlations see Vol. IV	185—238
New Routes for catalyst synthesis see Vol. IV	239—260
Cluster derived catalysts see Vol. V	261—264
Active phase-support interactions see Vol. V	265—318
Catalysis for synthesis of chemicals see Vol. V	319—360
Miscellaneous	
G. M. Schwab, München On the apparent compensation effect	361—363
H. Bock, Frankfurt am Main Banquet Toast	365—371

6010 B 1

Abundance and Reactivity of Surface Intermediates in Methanation, Determined with Transient-Kinetic Methods

C.-H. Yang, Y. Soong and P. Biloen
Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261, U.S.A.

Volume II, p. 3-14

Question (Professor H. Schulz, Karlsruhe/D)

Your observations pertain to CO hydrogenation to methane. I wonder what happens when the pathway shifts to Fischer-Tropsch synthesis of higher hydrocarbons and oxygenates, and what in your opinion would be the discriminating features.

Answer (P. Biloen)

Whereas transient-kinetic work on the cobalt-catalyzed F-T synthesis is in progress, the presently reported work does not contain information pertaining to your question. Drawing from what has been published so far, I would consider:

- . The ratio $\text{CH}_3\text{-ad}/\text{CH}_2\text{-ad}$ and the surface coverage in hydrogen as relevant parameters for the methane-versus-higher hydrocarbons selectivity;
- . The ratio $\text{CO-ad}/\text{CH}_2\text{-ad}$ as parameter for the oxygenates-versus-hydrocarbon selectivity.

Question (Professor J. Happel, New York, NY/U.S.A.)

(1) A number of studies indicate that direct dissociation of CO occurs at approximately the same rate as methanation. The influence of this step therefore should not be neglected, even if other steps are important.

(2) It may be useful to consider the methanation kinetics in terms of several rate-controlling steps, instead of one.

Answer (P. Biloen)

I agree with both statements. Statement (1) overlaps with the question raised by Professor Bartholomew (see below). With regard to your second statement it is relevant to notice that at our conditions holds: $R_4/R_- > 10^4$. There is, therefore, no reason why not several steps should obey:
 $r_+/r_- \gg 1$.

In the discussion we focussed on the nature of the first (most upstream in the reaction path) unidirectional step, and we put deliberately "the" between parenthesis (p. 12, line 12 from top).

Question (Professor C.H. Bartholomew, Provo-Utah/U.S.A.)

In a recent paper by Sughrue and Bartholomew (Appl. Catalysis, 1982) the kinetic data were shown to be consistent with a shift in the rate-determining step from CO dissociation at low temperature to carbon hydrogenation at high temperature. Thus, caution should be exercised in postulating one rate-determining step.

Answer (P. Biloen)

Your experimental results are consistent with other findings, as reported for example by Rabo, Risch and Poutsma (J. Catal. 53, 295, 1978). With regard to reaction conditions our work fits your "high temperature" domain. In addition, I agree fully that with changing temperature the relative rates of different elementary steps (have to) change.

The close similarity between your remark and Professor Happel's remarks to me indicates that we formulated in the paper our position unclearly. Allow me to recapitulate:

- . deliberately we utilize in our paper neither "rate-controlling" nor "rate-determining." We refer to a "unidirectional step," which corresponds to:

$$(r_+/r_-)_1 \gg 1$$

or, alternatively:

$$(\Delta G)_1 \ll 0$$

- . In order to interpret our transients we discuss the nature of the first (most upstream) unidirectional step and we propose: "oxygen removal." This is not necessarily identical to C-O bondrupture, nor do we wish to imply that there is only one essentially unidirectional step.

Question (Dr. G.A. Martin, Villeurbanne/F)

You rule out the possibility that surface blocking by inactive carbon limits the rate of CO dissociation. We recently proposed (J. Catal. 84, 45 (1983)) that CO dissociation requires a large ensemble of unblocked sites, and that, therefore, CO-ad itself inhibits the CO dissociation.

Answer (P. Biloen)

Your question can be rephrased as "What determines the rate of CO dissociation?" In our paper we rule out surface blocking by inactive carbon (a). We balance the two remaining possibilities, i.e., "intrinsic kinetics" (b) and "surface heterogeneity" (c) in favor of possibility (c). However, we mention also that we observe a kinetic H/D effect on θ , which points towards (b) (p. 13, paragraph 4). That was the position at the time of writing the manuscript (Fall 1983). Since then, and as reported at the Meeting, we confirmed the H/D effect: $\theta_{CD_x}/\theta_{CH_x} > 1.4$. This reinforces possibility(b), i.e., "intrinsic kinetics." You point towards "CO ad-inhibited CO dissociation," which is one of the intrinsic-kinetic effects which should be considered seriously.

Question (Professor A. Miyamoto, Nagoya/J)

We concluded from pulse surface reaction rate analysis (PSRA; J.P. C. 86, 2753 ('83); 87, 3648, 3652 ('83)) and from the observation of an inverse H/D effect that C-O bondrupture is being assisted by hydrogen. Why do you exclude a hydrogen-assisted C-O dissociation mechanism?

Answer (P. Biloen)

We do not exclude that CO is being hydrogenated before the C-O bond ruptures; we merely consider it to be unlikely, on the basis of what is being described as "circumstantial evidence" (p. 13, line 6 from top) which is being enumerated in ref. 15 to our paper.

We have confirmed your observation regarding an inverse H/D effect. However, we consider alternative explanations, such as a (thermodynamic) effect on θ_{CH_x} rather than θ_{CH_xO} , or an effect on Ni-O reduction (see below). Likewise, several interpretations can be given, in our opinion, to your interesting PSRA results. Their interpretation is particularly complicated by

the fact that θ_{CO} and θ_H vary sharply during the pulse. Which is the reason that we prefer to utilize isotopic transients.

Question (Professor D.A. Dowden/G.B.)

Why do you suppose that Al_2O_3 , TiO_{2-x} and MnO expedite the Ni_xO reduction?

Ni_xO is, if anything, basic but Al_2O_3 and TiO_{2-x} acidic (relatively), and MnO the least active of all middle transitional oxides in H_2 activation, although basic.

I would have expected Al_2O_3 and TiO_2 to stabilize Ni_xO and MnO to have no marked effect.

Answer (P. Biloen)

With our proposition we attempt to rationalize an observation: various extraneous oxides, which indeed are very different from the perspective of acid-base catalysis, all expedite the methanation.

There is a growing consensus in the literature, drawing from observations in homogeneous CO chemistry made by Shriver, as pointed out at the Meeting by Flambar, Sachtler and Vannice, that extraneous oxides provide Lewis-acid sites, activating CO at the metal-oxide interface. One of the problems with this concept is made manifest by your first remark: these oxides differ considerably in their acid-base properties. Another problem is, in our opinion, the proximity requirement implicit in (metal)-C-O-(cation) activation.

At the Meeting we proposed to consider, as an alternative, another potential bottleneck in the overall catalytic pathway: Ni_xO (re)reduction. CO dissociation probably requires cooperation of several contiguous Ni atoms, and therefore might be quite sensitive towards low steady-state concentrations of O^{2-}_{ad} and/or OH^-_{ad} .

Your remark regarding the Ni^{2+} stabilizing effect, for example via mixed-spinels, is well taken. However, we are presumably dealing with a predominantly metallic nickel surface, partially covered with extraneous ionic "clusters." What we propose to consider is that these extraneous ionic "clusters" destabilize $Ni^{6+}O^{5-}$ pairs. A Coulomb-interaction mechanism, for example, would

relax the proximity requirement implicit in the Lewis-site model. Isn't it after all the last rather than the first $O^{\delta-}$ which is difficult to remove from a metallic surface?

Remark (Professor D.L. Trimm, Kensington/Aus.)

Rockova and Trimm studied methanation on a range of catalysts (Proceedings, 7th Int. Congr. Catalysis, Tokyo, 1980), and found agreement with the suggestion that oxide reduction could be rate determining. Distinction from surface-oxide formation as the rate-determining step is difficult.

Answer (P. Biloen)

I appreciate your remark.

Remark (Professor C.H. Bartholomew, Provo-Utah/U.S.A.)

It is very interesting that you observe a ten times larger surface intermediates coverage on Raney Nickel relative to Ni/SiO_2 , since Uhen and Bartholomew (J. Catal. 45, 402, 1980) observed a factor ten higher specific activity for Raney Ni compared to unsupported, unpromoted nickel.

Answer (P. Biloen)

I appreciate your calling attention to this, reinforcing, observation.

Question (M.A. Vannice, University Park, PA/U.S.A.)

Ni/TiO_2 catalysts are much more active than Ni/SiO_2 catalysts for CO hydrogenation. Have you studied already Ni/TiO_2 , utilizing transient-kinetic techniques?

Answer (P. Biloen)

You point towards an obviously needed extension of the work reported at present. The answer to your question is "no," and the reason is that our rate-limiting (hopefully not: unidirectional) step is the acquisition of well-characterized (TOF, surface area measurement) materials. Which is an invitation.