PREPARATION OF CATALYSTS

Scientific Bases for the Preparation of Heterogeneous Catalysts

B. DELMON, P. A. JACOBS AND G. PONCELET (editors)

PREPARATION OF CATALYSTS TO THE PROPERTY OF TH

Scientific Bases for the Preparation of Heterogeneous Catalysts

Proceedings of the International Symposium held at the Solvay Research Centre, Brussels, October 14 –17, 1975

Editors

B.DELMON, P.A.JACOBS AND G.PONCELET



ELSEVIER SCIENTIFIC PUBLISHING COMPANY Amsterdam – Oxford – New York 1976 ELSEVIER SCIENTIFIC PUBLISHING COMPANY 335 Jan van Galenstraat P.O. Box 211, Amsterdam, The Netherlands

AMERICAN ELSEVIER PUBLISHING COMPANY, INC. 52 Vanderbilt Avenue New York, New York 10017

ISBN: 0-444-41428-2

Copyright © 1976 by Elsevier Scientific Publishing Company, Amsterdam

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher,

Elsevier Scientific Publishing Company, Jan van Galenstraat 335, Amsterdam

Printed in The Netherlands

This Symposium was organized by :

Division de Catalyse, Société Chimique de Belgique

ORGANIZING COMMITTEE OF THE SYMPOSIUM

Chairman

: B. DELMON, Professeur, Université
Catholique de Louvain; Président,
Division de Catalyse de la Société
Chimique de Belgique.

Secretaries

- : G. PONCELET, Université Catholique de Louvain.
 - P. JACOBS, Aangestelde Navorser N.F.W.O., Katholieke Universiteit Leuven.

Members

- : R. CAHEN, Chef de Division,
 Département Raffinage, LABOFINA.
 - R. COEKELBERGS, Professeur, Ecole Royale Militaire.
 - H. DEBUS, Directeur, Département Raffinage, LABOFINA.
 - W.L. DE KEYZER, Professeur, Université Libre de Bruxelles.
 - E. DEROUANE, Professeur, Facultés Notre-Dame de la Paix, Namur.
 - L. FIERMANS, Rijksuniversiteit, Gent.
 - G. FROMENT, Professor, Rijksuniversiteit
 Gent
 - A. HENDRICKX, Chef de Département, U.C.B.
 - A. JELLI, GLAVERBEL
 - P. LAMBERT, Directeur du Développement, U.C.B.
 - A. LECLOUX, Chef de Service, SOLVAY
 - G. L'HOMME, Professeur, Université de Liège.

- B.C. LIPPENS, Assistant Manager,
 TEXACO BELGIUM
- R. POUILLIART, Ingénieur Conseil, CARBOCHIMIQUE.
 - J.P. SCHURMANS, Technical Director, CATALYSIS AND CHEMICALS EUROPE.

ACKNOWLEDGEMENTS

It is a great pleasure for me to name here all those who have made this symposium possible, who have helped overcome the difficulties related to the impredictible growth in the number of registrants in the latest weeks before the symposium, and who, finally, have made everything run surprisingly smoothly in spite of this near overgrowth. It is really impossible to rank the various contributions according to their values. Please consider the order which has been adopted hereafter as completely stochastic.

In the name of the Organizing Committee and of the Société Chimique de Belgique, we thank those who have submitted papers, in such generous number (77 papers) that it turned out to be extremely difficult to select the ones best fitting the topics of the meeting. There were participants from 27 nations. We thank them too for having come here; but we also express our deep regret that the latest registrations could not be accepted.

We thank Solvay Company and its directors,
Dr. F. BLOYAERT and Mr. R. MORMONT, for the hospitality,
and Dr. A. LECLOUX for having supervised remarkably so
many arrangements and re-arrangements. The organization
of the department headed by Mr. A. GRODENT was responsible for Solvay's reception, projection, photography
and sound amplification. All participants will certainly
remember the smiling help of Mrs. A. LUGARIC and her
group: Miss J. THEYS, Mrs. M. DELPLANQUE, Miss N. MERTENS
and Mr. A. CALISTRI. Mr. A. ROGGEMAN was in charge of
projection and photography. Sound amplification was the
responsibility of Mr. L. ASSELBERGHS and Mr. C.DEROOSTER.
I wonder whether the most remarkable achievement is not
that of the Chef who prepared lunch for so many people

and who, with his numerous crew and the kind help of Solvay's reception team, made that the lunch lasted just one hour, allowing thus some relaxation before the afternoon session.

We also acknowledge the efficient and gracious help of our red-clad hostesses of the Public Relation of the Université Catholique de Louvain.

We thank LABOFINA S.A. for its support in printing so nicely the preprints and in achieving the printing of the list of registrants right in time. Mr. S. DEBRUX did not spare his efforts for that. Obviously, we shall not omit to cite Mr. L. SUETENS, whose artistic hobby is the origin of the small engraving representing the efficient and scientific production of impredictible animals. In addition to organising this printing, Dr. H. DEBUS and Dr. R. CAHEN have helped in numerous other aspects. We owe to Dr. R. CAHEN the organization of the special session on the Standardization of Catalyst Testing Methods. Dr. H. DEBUS and Dr. R. CAHEN conceived the project of the Vin d'Honneur and Cocktail Party and contacted the Catalyst Manufacturing Companies who generously offered this pleasant evening. In addition, I suspect that, together with our industrial friends from other companies, Dr. H. DEBUS and Dr. R. CAHEN contributed a lot to the fact that we had such a high proportion of participants from industry.

We acknowledge the support of the National Funds for Scientific Research of Belgium and of the Ministère de l'Education Nationale et de la Culture Française. This support is a testimony of the importance that those who are responsible for the scientific future of Belgium attach to the sort of symposium we have organized here. In addition to ICI Europe, Metallurgie Hoboken and UCB, Essochem and Procatalyse-Rhône-Poulenc have also accepted to support the symposium.

We thank all the lecturers, authors of communications and participants to discussions. The discussions were numerous and lively. We owe this success to the session attendants. Professor J.B. UYTTERHOEVEN's laboratory, of the Katholieke Universiteit Leuven, has accepted to share this burden with our group of Louvain-la-Neuve. The names of our devoted session attendants are listed below:

Dr. P. CANESSON, U.C.L.

Dr. M. COSTENOBLE, K.U.L.

Dr. M. DEBATTY-MESTDAGH, U.C.L.

Mr. W. DE WILDE, K.U.L.

Miss M.L. DUBRU, U.C.L.

Dr. P. GRANGE, U.C.L.

Mr. M. PORTENART, U.C.L.

Mr. L.J. VANDAMME, K.U.L.

Mr. J.M. ZABALA, U.C.L.

I thank also all colleagues from industry and belgian universities who have accepted to help us make the sessions run smoothly, by acting as session secretaries:

Dr. R. CAHEN (Labofina)

Dr. H. DEBUS (Labofina)

Prof. E.G. DEROUANE (Université de Namur)

Dr. A. FRENNET (Ecole Royale Militaire)

Dr. A. HENDRICKX (U.C.B.)

Dr. P. JACOBS (K.U.L.)

Dr. P. LAMBERT (U.C.B.)

Dr. A. LECLOUX (Solvay)

Prof. G. L'Homme (Université de Liège)

Prof. J.B. UYTTERHOEVEN (K.U.L.)

All participants got acquainted to our Symposium Secretaries, Dr. P. JACOBS, who so kindly and efficiently accomplished so many various tasks, and Dr. G. PONCELET, the thinking head of the whole system.

In the difficult circumstances resulting from a nearly overflooding of the Symposium by registrations, Dr. G. PONCELET has proved to be really a great organizer. We owe many thanks to Dr. P. JACOBS and Dr. G. PONCELET for their success.

Last, but not least, Mr. M. BULENS has helped edit and correct the greatest part of the discussion pages in the Symposium Proceedings. The Editors thank him heartily.

B. DELMON

Président Division de Catalyse Société Chimique de Belgique

FINANCIAL SUPPORT

The Organizing Committee gratefully acknowledges the "Ministère de l'Education Nationale et de la Culture Française" and the "Fonds National de la Recherche Scientifique - National Fonds voor Wetenschappelijk Onderzoek" for their financial support to the Symposium.

SOLVAY S.A. has accepted to host this Symposium and has generously provided numerous facilities. SOLVAY S.A. has given free disposal of the lecture room, dining rooms, reception lobby and surrounding space and has arranged sound amplification, projection, photocopying, photography and innumerable side services. Four persons of SOLVAY's staff have been permanently on the spot during the symposium.

LABOFINA S.A. has contributed to the costs of the printing of the announcing booklets and preprint volumes.

The Organizing Committee deeply thanks those two companies and gratefully acknowledges the financial support of the following Organisms and Companies:

Société Chimique de Belgique U.C.B. S.A. Essochem Research ICI Europe Rhone-Poulenc Chimie Fine Métallurgie Hoboken

Université Catholique de Louvain (U.C.L.) and its Public Relation Service (R.E.U.L.) has helped in many respects (hotel accomodation, busses) and has provided hostesses to the reception desk during the Symposium.

The Vin d'Honneur at the Town Hall of Brussels and the Cocktail were generously offered by the following Catalyst Manufacturers:

Akzo Chemie B.V. Ketjen Catalysts (The Netherlands),
BASF (Germany),
Catalyst and Chemicals Europe (Belgium),
Condea Petrochemie GmbH (Germany),
Cyanamid International (U.S.A.),
Engelhard Industries S.A. (Belgium),
Girdler - Südchemie Katalysator GmbH (Germany),
Grace Europe (France),
Johnson Matthey Chemicals Ltd. (England).

CONTENTS

| CONTENTS A SECRETARY OF A SECRETARY |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| The Committee of the state of t |
| The state of the s |
| Organizing Committee of the Symposium Acknowledgements |
| Determining mechanical properties of industrial catalysts: correlations with their morphological and physical-chemical properties (J.F. le Page and J. Miquel) |
| |
| Hydrocarbon conversion catalysts derived from synthetic alunite-type and jarosite-type crystal structures (R.W. Grose and E.M. Flanigen) 51 |
| The effect of preparation method on the acidity of mixed oxides (K. Tanabe, M. Itoh, K. Morishige and H. Hattori) |
| Effect of chemical composition, synthesis medium pH, and concentration of mother liquors on the nature of chromia-alumina catalysts (Z.G. Zulfugarov, S.H. Mamedova, A.I. Askerova and N.Yu. Mamed-Zade) |
| catalysts made by coprecipitation (E.J. Newson and J.V. Jensen) 91 |
| Preparation of copper and zinc chromium oxide catalysts for the reduction of fatty acid esters to alcohols (H. Boerma) |
| General synthesis methods for mixed oxide catalysts (P. Courty and C. Marcilly) |
| Factors that influence the preparation of pure molybdates and tungstates (F. Trifiró, P. Forzatti and P.L. Villa) |
| Influence of preparation and composition on multicomponent molybdate catalysts for the selective oxidation of olefins (M.W.J. Wolfs and J.H.C. van Hooff) |
| Catalysts for propene or isobutene oxidation to α, β -unsaturated aldehydes and acids (O.V. Isaev and L.Ya. Margolis) |

| oxidation and oxidative ammonolysis of heterocyclic and other compounds (E. Dziluma, S. Giller, V. Slavinska, V. Evgrashin, D. Kreile, |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A. Strautina and I. Milman) |
| The preparation and activation of SnO ₂ + Cr ₂ O ₃ catalysts (F. Solymosi, F. Bozsó and A. Hesz) |
| Some remarks on the preparation of alloy catalysts for selectivity studies (H.C. de Jongste, F.J. Kuijers and V. Ponec) |
| Scientific basis of catalyst preparation (G.K. Boreskov) |
| Effect of the impregnation conditions on the internal distribution of the active species in catalysts (J. Cervello, E. Hermana, J.F. Jiménez and F. Melo) |
| Application of electronic spectroscopy to the chemical characterization of iridium and palladium catalysts (F. Bozon-Verduraz, M. Tardy, G. Bugli, G. Pannetier and C. Leclère) |
| The effect of thermal ageing on metal crystallite growth and catalytic activity of supported platinum group metal catalysts (I.L. Dodgson and D.E. Webster) |
| The formation of disperse structure of an active component on the carrier surface in the process of preparation and activation of an impregnated catalyst (V.V. Kostrov, I.P. Kirillov, Y.F. Akulichev and V.A. Smirnov) |
| Textural and structural parameters influencing the ageing of Cu/ZnO L.T.S. catalysts (G. Leherte, R. Derie and P.H. Duvigneaud) 303 |
| Preparation and catalytic properties of supported metal or metal-oxide on inorganic oxide aerogels (M. Astier, A. Bertrand, D. Bianchi, A. Chenard, G.E.E. Gardes, G. Pajonk, M.B. Taghavi, S.J. Teichner and |
| B.L. Villemin) |
| Production of methanation catalysts (G.W. Bridger and C. Woodward) . 331 |
| The CoO-MoO ₃ -γ-Al ₂ O ₃ catalyst. Influence of the support. A review (V.H.J. de Beer and G.C.A. Schuit) |

| The preparation of MoO ₃ -CoO-Al ₂ O ₃ catalyst and its characteristics (Y. Kotera, K. Ogawa, M. Oba, K. Shimomura, M. Yonemura, A. Ueno |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| and N. Todo) |
| The activator system of oxidic hydrodesulfurization catalysts: |
| preparational aspects (R. Moné) |
| preparational aspects (it. Mone) |
| Physico-chemical interaction between Ni and support in the preparation |
| of Ni-Mo/Al ₂ O ₃ hydrogenolysis catalysts (H. Lafitau, E. Neel and |
| J.C. Clement) |
| Preparation, characterization and stability of molybdenum oxide |
| catalysts of the monolayer type (T. Fransen, P.C. van Berge and |
| P. Mars) |
| Study of the activation and thornal stability of abromia alumina |
| Study of the activation and thermal stability of chromia-alumina |
| catalysts (Y.S. Khodakov, V.I. Yakovlev, V.V. Zasypkin, |
| G.M. Panchenkov and Kh.M. Minachev) |
| Heterogeneous catalyst preparation: the fabrication of microstructures |
| (S.P.S. Andrew) |
| H. Conday) |
| Dispergation and mixing of oxide-base catalytic masses in the presence of |
| surfactants (U.G. Shirokov, I.P. Kirillov and S.P. Kochetkov) |
| (P.A Deany) |
| Preparation of an industrial nickel supported catalyst guided by |
| fundamental studies (J. Cosyns, M.T. Chenebaux, J.F. le Page and |
| R. Montarnal) |
| Maggian 1985 - State and State and Color Washington Color and State and Color |
| The influence of preparation methods on structural and catalytic properties of transition metal ions supported on alumina (M. Lo Jacono |
| and M. Schiavello) |
| The Market No. 1995 And Market No. 1995 And School St. |
| The influence of preparation parameters on the reactivity of Cr ^{II} surface |
| compounds (modified Phillips catalysts) (H.L. Krauss, B. Rebenstorf, |
| U. Westphal and D. Schneeweiss) |
| Effect of thermal pre-treatment conditions on platinum dispersity over |
| aluminium oxide and zeolites (V. Penchev, Ya. Neynska and |
| V Kanaginary) |
| V. Kanazirev) |
| Fig. 1. (estimated 1. The disputation Violating A. W.) |
| Role of tin in platinum-tin reforming catalysts (R. Bacaud, P. Bussière, |
| F. Figueras and J.P. Mathieu) |

| catalytic properties with the method of preparation (C. Betizeau, C. Bolivar, H. Charcosset, R. Frety, G. Leclerc, R. Maurel and |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| L. Tournayan) |
| Formation and inhibition of formation of compounds between deposited substance and oxidic carriers (G.T. Pott and W.H.J. Stork) |
| Effects of different factors on the specific surface area, activity, stability and mechanical strength of industrial catalysts (Kh.I. Areshidze and |
| G.O. Chivadze) |
| Factors determining the attrition of fluid-bed and coated catalysts (R. Haase, U. Illgen, J. Richter-Mendau and J. Scheve) |
| Promoted chromium-zinc-manganese oxide catalyst for decarbonylation reactions and scientific principles of its preparation (S.A. Hiller, A.Ya. Karmilchik, V.V. Stonkus, B.S. Katayev and M.V. Shymanska) . 579 |
| The preparation of the catalysts for methanol synthesis and their characteristics (Y. Kotera, M. Oba, K. Ogawa, K. Shimomura and |
| H. Uchida†) |
| Porous ceramic coatings on metal substrates as catalyst supports (P.J. Denny) |
| Catalysts for automobile emission control (J.W. Hightower) 615 |
| Metal-ceramic structures for catalytic conversion of exhaust gases (R. Lacroix) |
| The preparation of MnO_x on gamma-alumina acceptors for waste gas desulphurization (P.J.W.M. van den Bosch and W.A. de Jong) 651 |
| Polydispersive aluminium oxide as a catalyst carrier (S. Janiak and J. Wrzyszcz) |
| A study of the formation of titanium trichloride, a catalyst for stereospecific polymerization of propylene (V.A. Zakharov, |
| Ye. Ye. Vermel, S.G. Artamonova, P.A. Zhdan, N.G. Maximov, V.F. Anufrienko, V.M. Mastikhin and Yu.D. Pancratiev) 673 |
| List of participants |
| Author index |

At the moment the Organizing Committee had decided on the subject, the hope was that this Symposium could constitute a discussion of various scientific problems which are involved in the manufacture of real, industrially used, heterogeneous catalysts. Catalysts are solid materials or solid chemical products, possessing a high market value on a weight basis. The intention was to discuss in an international meeting the scientific domains on which the activity of an important, well distinct, branch of industry rests. The hope was that as little catalysis as possible would be mentioned. Indeed, the preparation of a solid material involves mainly solid state chemistry and adhesion phenomena. Since such a solid material has a complicated texture and a well-developped surface area, manufacture also implicates colloid chemistry and various interface phenomena in addition to adhesion, diffusion and mobility processes in the solids or at their surface. The technology involved is related to other fields, principally to the manufacture of ceramics, powder technology, surface treatments, technical realization of adhesive joints between metal and/or ceramics, materials technology, and cognate areas. The hope was that the symposium would help to define better the fundamental phenomena involved and the technical similarities. People in charge of the manufacture of catalysts are often catalysis-minded or at least are working in such an environment. Some extra-disciplinary contributions, as well. as multi-disciplinary approaches, are thus clearly necessary.

The goal of the symposium was certainly ambitious. It must be useful to evaluate its accomplishments (if any) and deficiencies.

YTEV SMEET IL LESS! I LESS TO THE STATE OF T

IS THE MANUFACTURE OF CATALYSTS CONCERNED WITH BASIC SCIENCE ?

A disappointment from this meeting (but not completely unexpected) has been that so few communications have been presented by industrial laboratories. There are two over-repeated explanations for this fact: (i) catalyst manufacturers

are reluctant to divulge secret preparation details, many of which are of paramount importance; (ii) catalyst fabrication is trial and error, foreman's know-how and tradition, and is not amenable to scientific analysis. Both explanations certainly contain their share of truth.

However, lobby and dinner conversation, even between competitors, usually goes well beyond what is said during sessions. To the outsider, it often seems that the first explanation is used as an apologizing escape.

Although fairly unaware of the industry's problems, researchers working in an academic environment commonly adhere to the second hypothesis. There is hardly any academic investigator who has not been faced with the extremely difficult problems of reproducing a catalyst, not only when undertaking to synthesize some formulation described in the literature, but also when preparing a second batch of his own catalyst. When attempting to decribe precisely the preparation technique in the experimental part of a scientific paper, the academic investigator invariably discovers that this description (i) is closer to a cooking recipe than to the product of a scientific approach (e.g. how can stirring be quantified: as moderate or high; why is a 1 hr ageing period necessary and longer or shorter times inadequate ?) and (ii) in spite of his efforts only conveys a small part of (probably) relevant information. Consequently, the cooking recipe, even casually read by some chef, will produce a valuable product, whereas the industrious ungifted people will not be helped much.

The second hypothesis, namely that making catalysts is art rather than science, finds additional support in the fact that the authors of many communications at the Symposium reported new and interesting effects and unexpected correlations, but had difficulties in interpreting them. It seems very likely that many authors, at the moment they propose a communication, discover that the number of their results which can be translated in conventional scientific words and could fit the traditional format of a scientific paper is substantially less than anticipated. For all investigators, academic as well as industrial, it may seem difficult to express publicly views,