

---

# **CHEMISTRY OF CATALYTIC PROCESSES**

---

**Bruce C. Gates  
James R. Katzer  
G. C. A. Schuit**

---

# CHEMISTRY OF CATALYTIC PROCESSES

---

**Bruce C. Gates**  
**James R. Katzer**  
**G. C. A. Schuit**

University of Delaware  
Center for Catalytic Science  
and Technology  
Department of Chemical Engineering

**McGraw-Hill Book Company**

New York St. Louis San Francisco Auckland Bogotá Düsseldorf  
Johannesburg London Madrid Mexico Montreal New Delhi  
Panama Paris São Paulo Singapore Sydney Tokyo Toronto

## CHEMISTRY OF CATALYTIC PROCESSES

Copyright © 1979 by McGraw-Hill, Inc. All rights reserved. Printed in the United States of America. 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.

4 5 6 7 8 9 0 FGRFGR 8 3 2 1 0

This book was set in Times Roman.

The editors were Rose Ciofalo, Douglas J. Marshall, and Bob Leap;  
the production supervisor was Milton J. Heiberg.

The drawings were done by Lorraine Turner and Judy Katzer.  
Fairfield Graphics was printer and binder.

### Library of Congress Cataloging in Publication Data

Gates, Bruce C

Chemistry of catalytic processes.

(McGraw-Hill series in chemical engineering)

Includes bibliographical references and index.

I. Catalysis. I. Katzer, James R., date joint  
author. II. Schuit, G. C. A., joint author. III. Title.

TP156.C35G37 660.2'995 77-16112

ISBN 0-07-022987-2

---

## McGraw-Hill Chemical Engineering Series

### Editorial Advisory Board

**James J. Carberry**, *Professor of Chemical Engineering, University of Notre Dame*  
**James R. Fair**, *Director, Engineering Technology, Monsanto Company, Missouri*  
**Max S. Peters**, *Dean of Engineering, University of Colorado*  
**William R. Schowalter**, *Professor of Chemical Engineering, Princeton University*  
**James Wei**, *Professor of Chemical Engineering, Massachusetts Institute of Technology*

---

### Building the Literature of a Profession

Fifteen prominent chemical engineers first met in New York more than fifty years ago to plan a continuing literature for their rapidly growing profession. From industry came such pioneer practitioners as Leo H. Baekeland, Arthur D. Little, Charles L. Reese, John V. N. Dorr, M. C. Whittaker, and R. S. McBride. From the universities came such eminent educators as William H. Walker, Alfred H. White, D. D. Jackson, J. H. James, Warren K. Lewis, and Harry A. Curtis. H. C. Parmelee, then editor of *Chemical and Metallurgical Engineering*, served as chairman and was joined subsequently by S. D. Kirkpatrick as consulting editor.

After several meetings, this committee submitted its report to the McGRAW-HILL Book Company in September 1925. In the report were detailed specifications for a correlated series of more than a dozen texts and reference books which have since become the McGRAW-HILL Series in Chemical Engineering and which became the cornerstone of the chemical engineering curriculum.

From this beginning there has evolved a series of texts surpassing by far the scope and longevity envisioned by the founding Editorial Board. The McGRAW-HILL Series in Chemical Engineering stands as a unique historical record of the development of chemical engineering education and practice. In the series one finds the milestones of the subject's evolution: industrial chemistry, stoichiometry, unit operations and processes, thermodynamics, kinetics, and transfer operations.

Chemical engineering is a dynamic profession, and its literature continues to evolve. McGRAW-HILL and its consulting editors remain committed to a publishing policy that will serve, and indeed lead, the needs of the chemical engineering profession during the years to come.

### The Series

**Bailey and Ollis:** *Biochemical Engineering Fundamentals*  
**Bennett and Myers:** *Momentum, Heat, and Mass Transfer*



**Beveridge and Schechter:** *Optimization: Theory and Practice*  
**Carberry:** *Chemical and Catalytic Reaction Engineering*  
**Churchill:** *The Interpretation and Use of Rate Data—The Rate Concept*  
**Clarke and Davidson:** *Manual for Process Engineering Calculations*  
**Coughanowr and Koppel:** *Process Systems Analysis and Control*  
**Danckwerts:** *Gas Liquid Reactions*  
**Gates, Katzer, and Schuit:** *Chemistry of Catalytic Processes*  
**Harriott:** *Process Control*  
**Johnson:** *Automatic Process Control*  
**Johnstone and Thring:** *Pilot Plants, Models, and Scale-up Methods in Chemical Engineering*  
**Katz, Cornell, Kobayashi, Poettmann, Vary, Elenbaas, and Weinaug:** *Handbook of Natural Gas Engineering*  
**King:** *Separation Processes*  
**Knudsen and Katz:** *Fluid Dynamics and Heat Transfer*  
**Lapidus:** *Digital Computation for Chemical Engineers*  
**Luyben:** *Process Modeling, Simulation, and Control for Chemical Engineers*  
**McCabe and Smith, J. C.:** *Unit Operations of Chemical Engineering*  
**Mickley, Sherwood, and Reed:** *Applied Mathematics in Chemical Engineering*  
**Nelson:** *Petroleum Refinery Engineering*  
**Perry and Chilton (Editors):** *Chemical Engineers' Handbook*  
**Peters:** *Elementary Chemical Engineering*  
**Peters and Timmerhaus:** *Plant Design and Economics for Chemical Engineers*  
**Reed and Gubbins:** *Applied Statistical Mechanics*  
**Reid, Prausnitz, and Sherwood:** *The Properties of Gases and Liquids*  
**Sherwood, Pigford, and Wilke:** *Mass Transfer*  
**Slattery:** *Momentum, Energy, and Mass Transfer in Continua*  
**Smith, B. D.:** *Design of Equilibrium Stage Processes*  
**Smith, J. M.:** *Chemical Engineering Kinetics*  
**Smith, J. M., and Van Ness:** *Introduction to Chemical Engineering Thermodynamics*  
**Thompson and Eckler:** *Introduction to Chemical Engineering*  
**Treybal:** *Liquid Extraction*  
**Treybal:** *Mass Transfer Operations*  
**Van Winkle:** *Distillation*  
**Volk:** *Applied Statistics for Engineers*  
**Walas:** *Reaction Kinetics for Chemical Engineers*  
**Wei, Russell, and Swartzlander:** *The Structure of the Chemical Processing Industries*  
**Whitwell and Toner:** *Conservation of Mass and Energy*

# CONTENTS

For  
Eva, Judy, and Jutta

## Introduction

### Processes

### Reactions

### Catalysis

### Analytic chemistry

### Cracking reactions

### Isomerization

### Yields, quality

### Cracking reactions

### Properties of cracking catalysts: Reaction mechanisms

### Characterization of activity, Mechanisms of cracking reactions, Carbonaceous deposits on surfaces, Details of cracking reactions

### Summary of cracking catalysts

### Cracking catalysts

### Isomerization

### Isomerization catalysts

### Properties and general properties, Chemical properties

### Catalytic reactions

### Introduction, Summary, X and Y catalysts, X and Y catalysts, X and Y catalysts, X and Y catalysts, X and Y catalysts

### Relations between surface properties and catalytic activity

### Surface chemistry, Zeolites

### Relationships of size, structure and zeolite catalysis

### Catalytic activity

### Catalytic activity

### Diffusion, adsorption and other catalytic properties

---

# PREFACE

---

Because of its economic importance, catalysis is one of the most intensely pursued subjects in applied chemistry and chemical engineering. It is complex, encompassing solid and surface structure, reaction mechanism, and analysis and design of chemical reactors. The complexity makes the subject difficult to teach and write about with depth and coherence, and most practitioners have learned their trade almost entirely from on-the-job training. We believe that there is need for a book about catalysis to convey what the science and practice of the subject are really like. We hope to have begun to meet this need by writing in detail about some of the most important industrial applications of catalysis, attempting to integrate the science and engineering in a way reflecting their integration in practice.

The book is not meant to be comprehensive but to provide a representative cross section of applied catalysis and some insight into catalytic practice. In particular, we have attempted to illustrate how the chemistry constrains the engineering design and how the design limitations, at the same time, restrict the choice of chemical variables such as catalyst composition. We hope that the book demonstrates the complexity of industrial catalysts, which have been developed through years of empirical testing to offer surfaces with combinations of functions just suited to the desired reactions.

There are five chapters, each concerned with an industrial process or class of processes, namely, catalytic cracking, transition-metal-complex catalysis, catalytic reforming, partial oxidation of hydrocarbons (as illustrated by ammoxidation), and hydrodesulfurization. The processes were chosen because they are industrially important and illustrate the major classes of catalysts: acids, transition metals, metal oxides, and metal sulfides. The sequence proceeds roughly from the best-understood to the least well understood chemistry. The coherence is intended to be provided by the chemistry rather than the engineering, and the engineering subjects are introduced as they arise in this context. We believe that there is value in the quantitative illustration of the engineering

methods, and our intention is that this book, with its summaries of the available processing data, will complement the existing books on chemical reaction engineering.

Each chapter is arranged roughly along the following lines: the process is introduced with a brief statement of the catalytic chemistry and process engineering; the chemistry is then presented in detail; and the engineering follows, with quantitative examples included to illustrate design methods.

The final manuscript evolved from notes for a graduate course and an intensive one-week short course taught at the University of Delaware. Believing that others may find this useful as a textbook, we have included problems with each chapter. The background information required for understanding the book includes standard undergraduate chemistry and the basic concepts of catalysis and chemical reaction engineering. Graduate students of chemical engineering and of technical chemistry should be adequately prepared for it, although an instructor's guidance will be helpful in directing students to the appropriate fundamentals for review. Students of chemistry who lack any experience with chemical engineering would profit from working through an introduction to reaction engineering such as Denbigh and Turner's "Chemical Reactor Theory," Cambridge University Press, 1971. Russell and Denn's "Introduction to Chemical Engineering Analysis," Wiley, 1972, is also recommended.

Without the help and criticisms of our students and colleagues, this book could not have been written. The comments of the industrial chemists and engineers who attended our annual short course have been especially helpful in eliminating errors and correcting false impressions of commercial practice. Many colleagues have helped us, and we especially thank W. H. Manogue, who offered invaluable comments, and J. H. Olson, who prepared the final section of Chap. 1, which is concerned with the reaction engineering of catalytic cracking. We are very grateful to our department chairman, A. B. Metzner, for his encouragement and stimulation during the preparation of the manuscript. We also acknowledge the Fulbright-Kommission in Bonn for the fellowship that allowed B. C. Gates time to work the manuscript into final form.

Bruce C. Gates  
James R. Katzer  
G. C. A. Schuit



# CONTENTS

<b>Preface</b>	<b>xv</b>
<b>1 Cracking</b>	<b>1</b>
Introduction	1
Processes	1
Reactions	5
Catalysts	5
Catalytic chemistry	6
Cracking reactions	6
Introduction	6
Thermal cracking	8
Catalytic cracking	10
Properties of carbonium ions / Reactions of carbonium ions /	
Characterization of acidity / Mechanisms of carbonium-ion	
reactions / Carbonium ions on surfaces / Details of catalytic	
cracking chemistry	
Summary of catalytic cracking chemistry	45
Cracking catalysts	46
Introduction	46
Amorphous catalysts	46
Preparation and general properties / Chemical properties	
Crystalline (Zeolite) catalysts	49
Introduction / Synthesis / X and Y zeolite structures / Cation	
positions in X and Y zeolites / Mordenite structure / Zeolite	
surface chemistry	
Relations between surface properties and catalytic activity	68
Silica-alumina / Zeolites	
Performance of Silica-Alumina and Zeolite catalysts	78
Catalyst activity	78
Catalyst selectivity	80
Diffusional limitations and shape-selective catalysis	85
	ix

Reaction engineering of catalytic cracking	89
The Riser-tube reactor	90
The regenerator	99
Notation	102
References	104
Problems	107

## 2 Catalysis by Transition-Metal Complexes: The Wacker, Vinyl Acetate, Oxo, Methanol Carbonylation, and Ziegler-Natta Processes 112

Introduction	112
Catalysts and processes	112
Chemical bonding in transition-metal complexes	114
Classification of ligands	115
Ligand surroundings of a metal	118
Frontier theory	120
Structures of catalytic complexes	124
Reactions and catalytic properties of organometallic complexes	126
Ligand exchange	126
Oxidative addition	127
The insertion reaction	127
Processes	128
The Wacker process: ethylene oxidation to acetaldehyde	128
Reactions and catalysts	128
Reaction kinetics	129
Product distribution	130
Reaction mechanism	130
Process design	135
Vinyl Acetate synthesis	137
Reactions and catalysts	137
Reaction kinetics	138
Reaction mechanism	138
Process design	139
The Oxo process: hydroformylation of olefins	140
Reactions and catalysts	140
Reaction kinetics	141
Product distribution	142
Reaction mechanism	144
Process design	146
Methanol carbonylation	147
Reaction and catalyst	147
Reaction kinetics	148
Product distribution	148
Reaction mechanism	148
Process design	150
The Ziegler-Natta process: stereospecific polymerization of $\alpha$ -olefins	150
Reactions and catalysts	150
Reaction kinetics	152

Product distribution	157
Reaction mechanism	158
Process design	166
Process engineering and multiphase reactors	170
Mass-transfer influence	170
Homogeneous catalysis	176
Multiphase reactors and catalyst design	176
Catalyst solutions in pores of solids	177
Catalysis by matrix-bound complexes	177
Notation	179
References	180
Problems	182
 <b>3 Reforming</b>	 <b>184</b>
Introduction	184
Reactions	184
Thermodynamics	187
Kinetics	188
Catalysts	189
Operating conditions	190
Reactor design	191
Catalytic chemistry	193
Transition metals and their catalytic activity	193
Introduction	193
Bonding in metals	194
Bonding at metal surfaces	201
Reactions of Chemisorbed species	206
Alloys	213
Phase behavior / Surface compositions / Electronic structures /	
Catalytic activity	
Theoretical considerations	227
Current research	235
Reforming catalysts	236
The metal	236
Preparation techniques / Dispersion of metals in supported	
catalysts / Effects of crystallite size and support on catalytic	
activity / Catalyst poisoning	
The Alumina support	249
Preparation / Oxides with cubic-close-packed structures /	
Positions of the $Al^{3+}$ and $H^+$ ions in the close-packed anion	
structures / The intermediate aluminum oxides / Acidity of	
aluminas	
Reforming reactions	260
Metal-catalyzed reactions	260
Hydrogenation-dehydrogenation reactions / Aromatization	
reactions / Isomerization, dehydrocyclization, and	
hydrogenolysis reactions	

<i>Alumina-catalyzed reactions</i>	275
<i>Isomerization / Hydrocracking</i>	
<i>Bifunctional catalysis of reforming reactions</i>	280
<i>The reaction scheme / Isomerization / Dehydrocyclization /</i>	
<i>Catalyst deactivation by carbonaceous residues</i>	
Process engineering	289
Catalyst design and operation	289
Reaction engineering	294
Introduction	294
Reactor modeling	294
Notation	311
References	313
Problems	318

## 4 Partial Oxidation of Hydrocarbons: The Ammoxidation of Propylene 325

Introduction	325
The chemistry of oxidation	329
Noncatalytic oxidation	329
Oxidation catalyzed by coordination complexes of transition metals	331
Oxidation catalyzed by surfaces of oxides	337
Hydrocarbon surface intermediates	337
Bonding of surface intermediates	341
Structures of oxide surfaces	343
The introduction of oxygen: the Mars-van Krevelen mechanism	344
Summary	349
Ammoxidation of Propylene	349
Catalysts	349
Reactions	350
Kinetics	351
Adsorption	352
The selectivity problem	354
Reaction mechanism: a simplified interpretation	356
Structures of ammoxidation catalysts	360
The $UO_3$ - $SbO_4$ catalyst	361
Reaction mechanisms on $USb_3O_{10}$	364
The $FeSbO_4$ catalyst	366
Bismuth molybdate catalysts	366
Structures of the active catalyst / The catalytically active	
bismuth molybdate / A comprehensive model of the reaction	
mechanism	377
Multicomponent molybdate catalysts	379
Summary of reaction chemistry	380
Process design	382
Processes and operating conditions	382
Separation processes	382
Reactor design	383

Notation	384
References	385
Problems	388
<b>5 Hydrodesulfurization</b>	<b>390</b>
Introduction	390
Feedstocks	391
Reactions	392
Catalysts	393
Processes	394
Catalytic chemistry	396
Reactions	396
<i>Introduction</i>	396
<i>Reaction networks</i>	396
<i>Kinetics</i>	402
<i>Simplified kinetics for industrial feedstocks</i>	408
Catalysts	411
<i>Structures of oxidic catalysts</i>	412
<i>Structures of sulfide catalysts</i>	415
<i>Catalytic sites</i>	419
<i>The mechanisms of reaction on promoted catalysts</i>	422
Process Engineering	426
Introduction	426
Residuum hydrodesulfurization processes	426
Coal hydrodesulfurization processes	431
Separation processes	431
Mass transfer	432
Fluid flow and mixing	433
Catalyst aging	437
Reactor stability	442
Notation	442
References	443
Problems	445
<b>Indexes</b>	<b>448</b>
Name Index	
Subject Index	



---

## CHAPTER ONE

---

# CRACKING

---

## INTRODUCTION

---

### PROCESSES

Most industrial reactions are catalytic, and many process improvements result from the discovery of better chemical routes, usually involving new catalysts. One of the largest scale catalytic processes practiced is *cracking*, the conversion of large petroleum molecules into smaller hydrocarbons, primarily in the gasoline range. In the United States cracking capacity exceeds 5 million barrels per day, and because the process has such a large production volume, years of research and development giving incremental improvements in gasoline yields have been highly profitable.

Cracking processes were first carried out in the absence of catalysts, but in the last four decades a series of continuously improved cracking catalysts has been applied, all of them solid acids. The most important advance in cracking technology in the last three decades has been the development of zeolite catalysts. These catalyze cracking so much more rapidly than the earlier catalysts like silica-alumina that the processes have had to be essentially redesigned. Instead of a large fluidized bed, the reactor is now a small tube. Catalyst particles are conveyed through it by rapidly flowing oil vapors, which stay in contact with the catalyst for only about 5 s. Catalytic cracking is the process considered first in this book

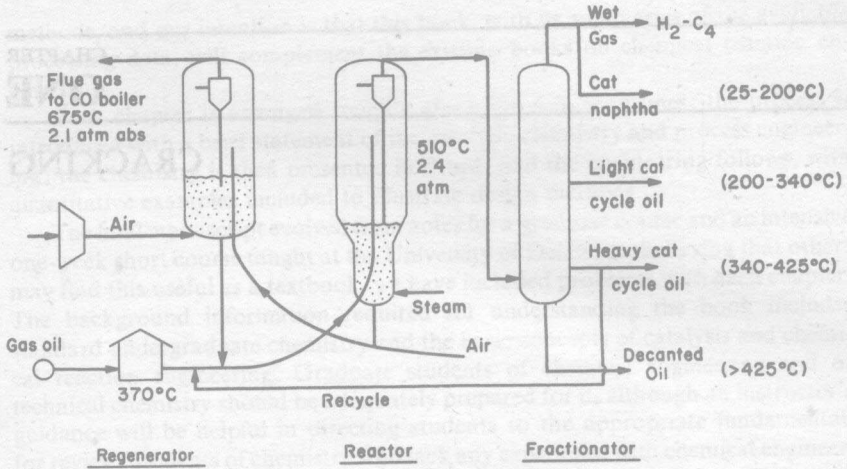


Figure 1-1 Flow diagram of catalytic-cracking process.

because cracking chemistry, unlike that of most catalytic processes, is well understood. It is the chemistry of strong acids, hydrocarbons, carbonium ions, and zeolites. The zeolite catalysts are familiar as molecular sieves, solids with crystal-

Table 1-1 Typical operating conditions for a catalytic cracking process

Riser-tube reactor	
Temperature, °C:	
Base	550
Top	510
Pressure, atm	3
Catalyst-to-oil ratio	6
Gas residence time, s	5-7
Regenerator	
Temperature in cyclone, °C	650-760
CO/CO <sub>2</sub> mole ratio	0.7-1.3:1
Pressure at bottom of fluidized bed, atm	3.5
Superficial gas velocity, cm/s	60
Solids residence time, s	30
Coke content of catalyst, wt. %	
At entrance	0.8
At exit	< 0.1

line structures including uniform, molecular-scale pores. They have well-known surface structures, whereas most solid catalysts, being amorphous, have poorly understood surface structures.

The details of the chemistry of catalytic cracking follow, but before they are introduced, the process is outlined so that the chemistry can be understood in the context of industrial practice. The process (Fig. 1-1) consists of a riser-tube reactor, a fluidized-bed disengaging unit for separating catalyst particles from product vapors, and a fluidized-bed regenerator, in which high-molecular-weight carbonaceous products, called *coke*, are burned off the catalyst to restore its activity. A fractionator downstream of the reactor and disengaging unit separates the product into various boiling fractions, and the heavy oil which has not undergone sufficient cracking is recycled to the reactor.

Typical operating conditions for the reactor and regenerator are summarized in Table 1-1, and typical product yields are collected in Table 1-2. These data provide a preliminary comparison between silica-alumina and zeolite catalysts.

One version of a riser-tube catalytic cracking unit is illustrated in Fig. 1-2. Gas oil is introduced with dispersive steam at the base of the reactor and mixed with regenerated catalyst supplied from a standpipe at the base of the fluidized-bed regenerator. The reactor diameter increases with height in this unit to maintain a nearly uniform catalyst velocity as the hydrostatic head in the riser

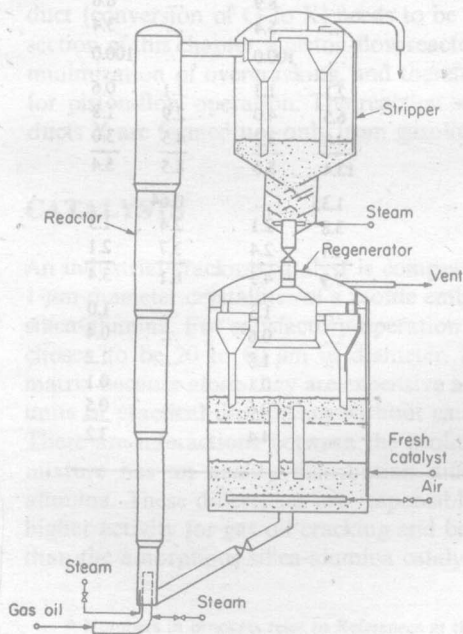


Figure 1-2 Riser catalytic-cracking unit.

**Table 1-2 Performance of commercial cracking reactors with silica-alumina and zeolite catalysts [1]**

Operating conditions	Durabead 5 <sup>a</sup>	Durabead 1 <sup>b</sup>
Vapor inlet temperature, °C	476	476
Catalyst inlet temperature, °C	548	549
Vapor outlet temperature, °C	474	471
Liquid hourly space velocity, vol/vol · h	1.0	0.9
Catalyst-to-oil ratio, vol/vol	1.9	2.0
Recycle ratio, vol recycle/vol fresh feed	0.84	0.82
Steam content of feed, wt %	3.6	3.5
Total reactor feed rate, bbl/day	12,900	13,400
Catalyst circulation rate, kg/h	136,065	136,065
Coke burnoff rate, kg/h	2,267	1,542
Boiling range of recycle stream, °C	215–332	232–327
Conversion, vol %	73.4	49.5
Cracking efficiency, 100 × vol gasoline/vol converted	77.6	77.3

	Yields			
	vol %	wt %	vol %	wt %
Synthetic tower bottoms	13.7	15.2	21.3	22.3
Distillate fuel oil	12.9	13.3	29.2	29.4
C <sub>4</sub> -free gasoline	56.9	48.7	38.3	32.9
Butanes	13.4	8.5	8.5	5.4
Dry gas (C <sub>3</sub> and lighter)	...	8.9	...	6.6
Coke	...	5.4	...	3.4
Total	...	100.0	...	100.0
<i>n</i> -Butane	2.1	1.3	1.1	0.6
Isobutane	6.5	4.0	2.9	1.8
Butenes	4.8	3.2	4.5	3.0
Total C <sub>4</sub>	13.4	8.5	8.5	5.4
<i>i</i> C <sub>4</sub> /C <sub>4</sub> ratio	1.35	...	0.64	...
Propane	3.8	2.1	2.4	1.3
Propylene	4.1	2.4	3.7	2.1
Total	7.9	4.5	6.1	3.4
Ethane	...	1.3	...	1.0
Ethylene	...	0.6	...	0.4
Methane	...	1.8	...	1.2
Hydrogen	...	0.1	...	0.1
Hydrogen sulfide	...	0.6	...	0.5
Total C <sub>2</sub> and lighter	...	4.4	...	3.2

<sup>a</sup> REHY zeolite in silica-alumina matrix.<sup>b</sup> Silica-alumina.