

## Contents

|            |                                                                                                       |  |
|------------|-------------------------------------------------------------------------------------------------------|--|
|            | <b>Volume 6</b>                                                                                       |  |
|            | <b>Preface</b> V                                                                                      |  |
|            | <b>List of Contributors</b> XVII                                                                      |  |
| <b>13</b>  | <b>Energy-Related Catalysis</b> 2677                                                                  |  |
| 13.1       | Perspectives in Oil Refining 2677<br><i>Patrick Sarrazin, Colin Baudouin, and<br/>Germain Martino</i> |  |
| 13.1.1     | Introduction 2677                                                                                     |  |
| 13.1.1.1   | Goals in Oil Refining 2677                                                                            |  |
| 13.1.1.2   | Scope of this Chapter 2677                                                                            |  |
| 13.1.2     | Oil Refining Today 2677                                                                               |  |
| 13.1.2.1   | Crude Oil Production and Market<br>Localization 2677                                                  |  |
| 13.1.2.2   | Product Quantities and Qualities 2679                                                                 |  |
| 13.1.2.3   | Refineries 2679                                                                                       |  |
| 13.1.2.4   | Processes and Catalysts 2681                                                                          |  |
| 13.1.3     | Future Refining Needs 2683                                                                            |  |
| 13.1.3.1   | Driving Forces 2683                                                                                   |  |
| 13.1.3.1.1 | Issues Associated with Crude<br>Supply 2683                                                           |  |
| 13.1.3.1.2 | Issues Linked with Product Demand 2683                                                                |  |
| 13.1.3.1.3 | Refinery Emissions 2685                                                                               |  |
| 13.1.3.2   | Future Refining 2685                                                                                  |  |
| 13.1.3.2.1 | Conversion 2685                                                                                       |  |
| 13.1.3.2.2 | Gasoline Manufacture 2686                                                                             |  |
| 13.1.3.2.3 | Clean Diesel Oil Production 2689                                                                      |  |
| 13.1.3.2.4 | Refinery Emissions Control 2692                                                                       |  |
| 13.1.3.2.5 | Catalyst Disposal 2692                                                                                |  |
| 13.1.4     | Conclusions 2693                                                                                      |  |
| 13.1.4.1   | Future Trends in Refining 2693                                                                        |  |
| 13.1.4.2   | Future Trends in Catalysis 2694                                                                       |  |
|            | References 2694                                                                                       |  |
| 13.2       | Hydrotreating 2695<br><i>Roel Prins</i>                                                               |  |
| 13.2.1     | Introduction 2695                                                                                     |  |
| 13.2.2     | Reaction Mechanisms 2696                                                                              |  |
| 13.2.2.1   | Hydrodesulfurization 2696                                                                             |  |
| 13.2.2.2   | Hydrodenitrogenation 2698                                                                             |  |
| 13.2.2.3   | Hydrodeoxygenation 2700                                                                               |  |
| 13.2.2.4   | Hydrodechlorination 2700                                                                              |  |
| 13.2.2.5   | Hydrotreating of Mixtures 2701                                                                        |  |
| 13.2.2.6   | The C–X Bond Breaking<br>Mechanism 2702                                                               |  |
| 13.2.3     | Catalyst Structure 2703                                                                               |  |
| 13.2.3.1   | Structure of the Oxidic Catalyst<br>Precursor 2703                                                    |  |
| 13.2.3.2   | Structure of the Sulfidic Catalyst 2704                                                               |  |
| 13.2.3.2.1 | Structure of Mo 2704                                                                                  |  |
| 13.2.3.2.2 | Structure of the Promoter 2705                                                                        |  |
| 13.2.3.2.3 | Surface Sites 2707                                                                                    |  |
| 13.2.3.2.4 | Modifiers 2708                                                                                        |  |
| 13.2.4     | Structure–Reactivity Relations 2709                                                                   |  |
| 13.2.5     | Hydrotreating Technology 2710                                                                         |  |
| 13.2.5.1   | Catalysts 2710                                                                                        |  |
| 13.2.5.2   | Reactor Systems 2711                                                                                  |  |
| 13.2.5.3   | FCC Naphtha Hydrotreating 2711                                                                        |  |
| 13.2.5.3.1 | Direct Hydrotreating 2711                                                                             |  |
| 13.2.5.3.2 | Pre- or Post-octane Upgrading 2714                                                                    |  |
| 13.2.5.4   | Diesel Hydrotreating 2714                                                                             |  |
| 13.2.5.5   | Other Desulfurization Technologies 2715                                                               |  |
| 13.2.6     | The Future of Hydrotreating 2715                                                                      |  |
|            | References 2716                                                                                       |  |
| 13.3       | Hydrodemetalation 2718<br><i>James Wei</i>                                                            |  |
| 13.3.1     | Introduction 2718                                                                                     |  |
| 13.3.2     | Metal Compounds in Petroleum 2719                                                                     |  |
| 13.3.3     | Residue Hydrotreating Technology 2720                                                                 |  |
| 13.3.4     | Reaction Kinetics and Diffusion<br>in Catalytic Hydrodemetalation 2721                                |  |
| 13.3.4.1   | Model Compound Kinetic Studies 2722                                                                   |  |
| 13.3.4.2   | Model Compound Diffusion 2723                                                                         |  |
| 13.3.4.3   | Intraparticle Metal Deposition<br>Profiles 2724                                                       |  |

|            |                                                                                                                                       |      |            |                                                                                         |      |
|------------|---------------------------------------------------------------------------------------------------------------------------------------|------|------------|-----------------------------------------------------------------------------------------|------|
| 13.3.4.4   | Hydrodemetalation of Petroleum Oils and Residua                                                                                       | 2724 | 13.5.3.4.3 | Metals: Ni, V, Na and Fe                                                                | 2750 |
| 13.3.5     | Catalyst Deactivation                                                                                                                 | 2725 | 13.5.3.4.4 | Sulfur                                                                                  | 2753 |
| 13.3.6     | Conclusions                                                                                                                           | 2727 | 13.5.3.4.5 | Nitrogen                                                                                | 2753 |
|            | References                                                                                                                            | 2727 | 13.5.4     | The Chemistry of Catalytic Cracking                                                     | 2753 |
| 13.4       | Catalytic Reforming                                                                                                                   | 2728 | 13.5.4.1   | Carbocations                                                                            | 2754 |
|            | <i>Mark D. Moser and Paula L. Bogdan</i>                                                                                              |      | 13.5.4.2   | Formation of Carbocations                                                               | 2755 |
| 13.4.1     | Introduction                                                                                                                          | 2728 | 13.5.4.3   | Isomerization Reactions                                                                 | 2755 |
| 13.4.2     | The Chemistry of Reforming                                                                                                            | 2730 | 13.5.4.4   | Carbon—Carbon Bond Breaking by Beta-Scission                                            | 2756 |
| 13.4.2.1   | Feed Composition and Characteristics                                                                                                  | 2730 | 13.5.4.5   | Hydride Transfer (also Referred to as Hydrogen Transfer)                                | 2756 |
| 13.4.2.2   | Reforming Products                                                                                                                    | 2730 | 13.5.4.6   | Heteroatom Chemistry: Sulfur                                                            | 2758 |
| 13.4.2.3   | Reforming Reactions                                                                                                                   | 2731 | 13.5.5     | FCC Catalysts                                                                           | 2758 |
| 13.4.3     | Reforming Catalysts                                                                                                                   | 2733 | 13.5.5.1   | Description and Formulation                                                             | 2758 |
| 13.4.3.1   | General Aspects                                                                                                                       | 2733 | 13.5.5.2   | Zeolite Component                                                                       | 2759 |
| 13.4.3.2   | Catalyst Regeneration                                                                                                                 | 2735 | 13.5.5.2.1 | Zeolite Modifications                                                                   | 2759 |
| 13.4.4     | Reforming Processes                                                                                                                   | 2735 | 13.5.5.2.2 | Zeolite Activity and Selectivity Effects                                                | 2760 |
| 13.4.4.1   | Process Variables                                                                                                                     | 2735 | 13.5.5.3   | Matrix                                                                                  | 2762 |
| 13.4.4.2   | Commercial Catalysts                                                                                                                  | 2736 | 13.5.5.3.1 | Commercial Matrices                                                                     | 2763 |
| 13.4.4.3   | Modeling/Optimization of Commercial Reforming Units                                                                                   | 2737 | 13.5.5.3.2 | Effect of Matrix on Selectivity                                                         | 2764 |
| 13.4.4.4   | Process Flow Schemes                                                                                                                  | 2738 | 13.5.5.4   | Characterization                                                                        | 2765 |
| 13.4.4.5   | Future Developments                                                                                                                   | 2740 | 13.5.5.5   | ZSM-5 Additives                                                                         | 2766 |
|            | References                                                                                                                            | 2740 | 13.5.6     | FCCU Environmental Emissions Controls                                                   | 2766 |
| 13.5       | Fluid Catalytic Cracking                                                                                                              | 2741 | 13.5.6.1   | Overview – Catalyst Versus Hardware                                                     | 2766 |
|            | <i>Wu-Cheng Cheng, E. Thomas Habib Jr., Kuppaswamy Rajagopalan, Terry G. Roberie, Richard F. Wormsbecher, and Michael S. Ziebarth</i> |      | 13.5.6.2   | Particulates                                                                            | 2768 |
| 13.5.1     | Introduction and Overview                                                                                                             | 2741 | 13.5.6.3   | Carbon Monoxide (CO)                                                                    | 2769 |
| 13.5.1.1   | History                                                                                                                               | 2741 | 13.5.6.4   | Sulfur Oxides (SO <sub>x</sub> )                                                        | 2769 |
| 13.5.1.2   | FCC Today                                                                                                                             | 2742 | 13.5.6.5   | Nitrogen Oxides (NO <sub>x</sub> )                                                      | 2770 |
| 13.5.1.3   | Position in a Modern Petroleum Refinery                                                                                               | 2743 | 13.5.7     | Laboratory Evaluations and Pilot Plant Testing                                          | 2770 |
| 13.5.1.4   | Environmental Issues                                                                                                                  | 2744 | 13.5.7.1   | Accelerated Aging of Catalysts                                                          | 2770 |
| 13.5.2     | FCC Unit Hardware and Operations                                                                                                      | 2745 | 13.5.7.2   | Simulation of Metals Poisoning                                                          | 2771 |
| 13.5.2.1   | Unit Types                                                                                                                            | 2745 | 13.5.7.3   | Reactor Types – Fixed Bed vs. Fluid Bed vs. Transport Phase                             | 2772 |
| 13.5.2.2   | Heat Balance                                                                                                                          | 2745 | 13.5.7.4   | Temperature Profile and Isothermal vs. Adiabatic Testing                                | 2773 |
| 13.5.2.3   | Modes of Operation                                                                                                                    | 2745 | 13.5.8     | Summary and Future Trends in Catalytic Cracking                                         | 2773 |
| 13.5.2.3.1 | Regeneration Mode – Partial Burn vs. Full Burn                                                                                        | 2745 |            | References                                                                              | 2775 |
| 13.5.2.3.2 | Resid Processing                                                                                                                      | 2746 | 13.6       | Hydrocracking and Catalytic Dewaxing                                                    | 2778 |
| 13.5.2.3.3 | Petrochemical Mode (Light Olefins)                                                                                                    | 2746 |            | <i>J. A. Rob van Veen, Johannes K. Minderhoud, Laurent G. Huve, and Wim H. J. Stork</i> |      |
| 13.5.3     | FCC Feeds                                                                                                                             | 2746 | 13.6.1     | Introduction                                                                            | 2778 |
| 13.5.3.1   | Sources and Trends                                                                                                                    | 2746 | 13.6.2     | Hydrocracking                                                                           | 2779 |
| 13.5.3.2   | Molecular Types                                                                                                                       | 2746 | 13.6.2.1   | Processes and Process Configurations                                                    | 2779 |
| 13.5.3.3   | Characterization                                                                                                                      | 2747 | 13.6.2.1.1 | Two-Stage Hydrocracking                                                                 | 2779 |
| 13.5.3.4   | Effects on FCC Unit Operation                                                                                                         | 2750 | 13.6.2.1.2 | Single-Stage Hydrocracking                                                              | 2780 |
| 13.5.3.4.1 | Conradson Carbon and Feed Heaviness                                                                                                   | 2750 |            |                                                                                         |      |
| 13.5.3.4.2 | Feedstock Composition                                                                                                                 | 2750 |            |                                                                                         |      |

|            |                                                                                                    |      |            |                                                                                              |      |
|------------|----------------------------------------------------------------------------------------------------|------|------------|----------------------------------------------------------------------------------------------|------|
| 13.6.2.1.3 | Alternative Process Schemes                                                                        | 2781 | 13.7.5.1   | Octane Numbers and Thermodynamic Equilibrium Concentrations of Isomeric Pentanes and Hexanes | 2818 |
| 13.6.2.1.4 | Mild Hydrocracking                                                                                 | 2782 | 13.7.5.2   | Processes for Isomerization of Pentanes and Hexanes                                          | 2819 |
| 13.6.2.1.5 | Reactor Design Aspects                                                                             | 2782 | 13.7.5.2.1 | Processes Using Aluminum Chloride/Hydrochloric Acid as Monofunctional Catalyst               | 2819 |
| 13.6.2.2   | Feedstocks                                                                                         | 2783 | 13.7.5.2.2 | Processes Using Bifunctional Catalysts Consisting of Pt Supported on Chlorinated Alumina     | 2821 |
| 13.6.2.3   | Products                                                                                           | 2784 | 13.7.5.2.3 | Processes Using a Noble Metal on Amorphous Silica–Alumina as Bifunctional Catalyst           | 2822 |
| 13.6.2.4   | Catalyst Systems                                                                                   | 2784 | 13.7.5.2.4 | Processes Using a Noble Metal on Zeolite as Bifunctional Catalyst                            | 2823 |
| 13.6.2.4.1 | HC Catalyst Design Rules                                                                           | 2786 | 13.7.5.3   | Combining C <sub>5</sub> and C <sub>6</sub> Alkane Isomerization with Physical Separations   | 2823 |
| 13.6.2.4.2 | Coke Deactivation                                                                                  | 2788 | 13.7.6     | Processes for Isomerization of Higher Alkanes                                                | 2826 |
| 13.6.2.4.3 | Zeolite-Based Catalysts                                                                            | 2789 | 13.7.7     | Processes for Conversion of <i>n</i> -Butane to Isobutane                                    | 2827 |
| 13.6.2.4.4 | Effect of Recycle Operation                                                                        | 2792 | 13.7.8     | Role of Alkane Isomerization in the Hydrocarbon Processing Industry                          | 2828 |
| 13.6.2.4.5 | New Catalyst Developments                                                                          | 2792 |            | References                                                                                   | 2828 |
| 13.6.2.5   | Ring Opening                                                                                       | 2794 |            |                                                                                              |      |
| 13.6.3     | Catalytic Dewaxing                                                                                 | 2794 |            |                                                                                              |      |
| 13.6.3.1   | Commercial Developments                                                                            | 2795 |            |                                                                                              |      |
| 13.6.3.2   | Shape-Selective Catalysis                                                                          | 2795 |            |                                                                                              |      |
| 13.6.3.3   | Dewaxing Catalysts                                                                                 | 2798 |            |                                                                                              |      |
| 13.6.3.3.1 | Reaction Pathway                                                                                   | 2798 |            |                                                                                              |      |
| 13.6.3.3.2 | Process Line-Ups                                                                                   | 2798 |            |                                                                                              |      |
| 13.6.3.3.3 | Cracking Dewaxing                                                                                  | 2801 |            |                                                                                              |      |
| 13.6.3.3.4 | Isomerization Dewaxing                                                                             | 2803 |            |                                                                                              |      |
| 13.6.3.4   | Future Trends in Catalytic Dewaxing – the Gas to Liquid Route                                      | 2804 |            |                                                                                              |      |
|            | References                                                                                         | 2805 |            |                                                                                              |      |
| 13.7       | Isomerization                                                                                      | 2809 |            |                                                                                              |      |
|            | <i>Swan Tiong Sie</i>                                                                              |      |            |                                                                                              |      |
| 13.7.1     | Introduction                                                                                       | 2809 | 13.8       | Alkylation of Isobutane with Light Alkenes on Solid Catalysts                                | 2830 |
| 13.7.2     | Mechanism of Skeletal Isomerization of C <sub>5</sub> + Alkanes with Acid Catalysts                | 2809 |            | <i>Yvonne Traa and Jens Weitkamp</i>                                                         |      |
| 13.7.2.1   | Reaction Cycle in Isomerization of Alkanes                                                         | 2809 | 13.8.1     | Introduction                                                                                 | 2830 |
| 13.7.2.2   | The Isomerization Reaction: Rearrangement of the Intermediate Carbenium Ion                        | 2809 | 13.8.2     | Stoichiometry of the Alkylation of Isobutane with Light Alkenes                              | 2830 |
| 13.7.2.3   | Supporting Evidence for the Protonated Cyclopropane (PCP) Isomerization Mechanism                  | 2811 | 13.8.3     | Role of Isobutane/Butene Alkylation in Petroleum Refining                                    | 2831 |
| 13.7.2.3.1 | Reactions with <i>n</i> -Butane                                                                    | 2811 | 13.8.4     | Salient Features of Isobutane/Alkene Alkylation on Solid Catalysts                           | 2834 |
| 13.7.2.3.2 | Effect of Chain Length on the Relative Rates of Isomerization of <i>n</i> -Alkanes                 | 2811 | 13.8.5     | Mechanistic Considerations                                                                   | 2838 |
| 13.7.2.3.3 | Location of Branching in Isomerized Alkanes                                                        | 2811 | 13.8.6     | Investigation of the Carbonaceous Deposits                                                   | 2843 |
| 13.7.2.4   | Chain Termination Reactions: Catalyst Deactivation                                                 | 2813 | 13.8.7     | Alkylation in the Supercritical Phase: <i>In Situ</i> Regeneration of Spent Catalysts?       | 2844 |
| 13.7.2.5   | Acid-catalyzed Cracking and Isomerization: Effect of Chain Length on Selectivity for Isomerization | 2814 | 13.8.8     | <i>Ex situ</i> Regeneration of Spent Catalysts                                               | 2845 |
| 13.7.3     | Mechanism of C <sub>4</sub> Alkane Isomerization                                                   | 2815 | 13.8.9     | Integral Yields of Alkylate                                                                  | 2848 |
| 13.7.4     | Isomerization Catalysts                                                                            | 2816 | 13.8.10    | Process Developments                                                                         | 2848 |
| 13.7.4.1   | Monofunctional Acidic Catalysts                                                                    | 2816 | 13.8.11    | Conclusions                                                                                  | 2850 |
| 13.7.4.2   | Bifunctional Catalysts                                                                             | 2817 |            | References                                                                                   | 2851 |
| 13.7.5     | Isomerization of Pentanes and Hexanes for Octane Enhancement                                       | 2818 | 13.9       | Oligomerization                                                                              | 2854 |
|            |                                                                                                    |      |            | <i>Cyril T. O'Connor</i>                                                                     |      |
|            |                                                                                                    |      | 13.9.1     | Introduction                                                                                 | 2854 |
|            |                                                                                                    |      | 13.9.2     | Background                                                                                   | 2855 |

|             |                                                   |      |             |                                                               |      |
|-------------|---------------------------------------------------|------|-------------|---------------------------------------------------------------|------|
| 13.9.3      | Fundamentals                                      | 2855 | 13.10.7.4   | Conversion of MTBE Plants for ETBE Production                 | 2875 |
| 13.9.3.1    | Mechanism of Alkene Oligomerization               | 2855 | 13.10.7.5   | Processes for TAME Production                                 | 2876 |
| 13.9.3.2    | Thermodynamics of Alkene Oligomerization          | 2857 | 13.10.7.6   | Multipurpose Processes for Production of Ethers               | 2877 |
| 13.9.3.3    | Kinetics of Alkene Oligomerization                | 2857 | 13.10.8     | Diesel Ethers                                                 | 2877 |
| 13.9.4      | Catalysts Used in Alkene Oligomerization          | 2858 | 13.10.8.1   | Dimethyl Ether                                                | 2877 |
| 13.9.4.1    | Zeolites                                          | 2858 | 13.10.8.1.1 | Properties of Dimethyl Ether                                  | 2877 |
| 13.9.4.2    | Mesoporous Catalysts                              | 2860 | 13.10.8.1.2 | Processes for Dimethyl Ether Production                       | 2878 |
| 13.9.4.3    | Other Acid Catalysts                              | 2860 | 13.10.8.2   | Di- <i>n</i> -Pentyl Ether                                    | 2879 |
| 13.9.4.4    | Catalysts Incorporating Metals                    | 2860 | 13.10.9     | The Future                                                    | 2879 |
| 13.9.5      | Industrial Applications of Alkene Oligomerization | 2860 |             | References                                                    | 2879 |
| 13.9.5.1    | Zeolite-Based Processes                           | 2860 | 13.11       | Steam Reforming                                               | 2882 |
| 13.9.5.2    | Catpoly Process                                   | 2862 |             | <i>Jens Richard Rostrup-Nielsen</i>                           |      |
| 13.9.5.3    | Dimerization Processes                            | 2862 | 13.11.1     | Introduction                                                  | 2882 |
| 13.9.6      | Conclusions                                       | 2863 | 13.11.1.1   | Reactions                                                     | 2882 |
|             | References                                        | 2863 | 13.11.1.2   | Thermodynamics                                                | 2882 |
|             |                                                   |      | 13.11.1.3   | Applications                                                  | 2883 |
| 13.10       | Etherification                                    | 2864 | 13.11.1.4   | Industrial Developments                                       | 2885 |
|             | <i>A. Outi I. Krause and Kari I. Keskinen</i>     |      | 13.11.2     | The Reforming Process                                         | 2886 |
| 13.10.1     | Scope                                             | 2864 | 13.11.2.1   | The Tubular Reformer                                          | 2886 |
| 13.10.2     | Introduction and History of Tertiary Ethers       | 2864 | 13.11.2.2   | Convective Reformers                                          | 2888 |
| 13.10.3     | Chemistry                                         | 2865 | 13.11.2.3   | Reforming Rates and New Reformer Concepts                     | 2888 |
| 13.10.3.1   | Main Etherification Reactions                     | 2865 | 13.11.3     | Catalysts                                                     | 2890 |
| 13.10.3.2   | Most Important Side Reactions                     | 2866 | 13.11.3.1   | Catalyst Activity                                             | 2890 |
| 13.10.3.3   | Thermodynamics of Ether Reactions                 | 2866 | 13.11.3.2   | Non-Metal Catalysts                                           | 2891 |
| 13.10.3.4   | Kinetic Models                                    | 2868 | 13.11.3.3   | Kinetics                                                      | 2892 |
| 13.10.4     | Other Ethers                                      | 2868 | 13.11.3.4   | Industrial Catalysts                                          | 2893 |
| 13.10.4.1   | Heavier Ethers                                    | 2868 | 13.11.4     | Major Catalyst Problems                                       | 2894 |
| 13.10.4.1.1 | C <sub>8</sub> Alkenes                            | 2868 | 13.11.4.1   | Sintering                                                     | 2894 |
| 13.10.4.1.2 | Higher Alcohols                                   | 2868 | 13.11.4.2   | Sulfur Poisoning                                              | 2895 |
| 13.10.4.2   | Polyfunctional Ethers                             | 2870 | 13.11.4.3   | Carbon Formation                                              | 2896 |
| 13.10.5     | Catalysts                                         | 2870 | 13.11.4.4   | Catalyst Promotion                                            | 2899 |
| 13.10.5.1   | Acidic Ion-Exchange Resins                        | 2870 | 13.11.5     | The Active Site                                               | 2900 |
| 13.10.5.2   | Zeolites and Modified Zeolites                    | 2872 | 13.11.5.1   | Step Sites                                                    | 2900 |
| 13.10.5.3   | Other Acidic Catalysts                            | 2872 | 13.11.5.2   | Carbon Formation                                              | 2901 |
| 13.10.5.4   | Catalyst Deactivation                             | 2872 | 13.11.5.3   | Blockage of Step Sites                                        | 2901 |
| 13.10.6     | Raw Materials and Products                        | 2873 | 13.11.5.4   | Geometric and Electronic Effects                              | 2902 |
| 13.10.6.1   | Typical Raw Materials                             | 2873 |             | References                                                    | 2903 |
| 13.10.6.2   | Feed Stream Treatment                             | 2873 | 13.12       | Water Gas Shift and COS Removal                               | 2905 |
| 13.10.6.3   | Ether Products                                    | 2874 |             | <i>Kai-Olaf Hinrichsen, Karl Kochloeff, and Martin Muhler</i> |      |
| 13.10.6.4   | Hydrocarbon Products                              | 2874 | 13.12.1     | Introduction                                                  | 2905 |
| 13.10.7     | Processes                                         | 2874 | 13.12.2     | Thermodynamics                                                | 2906 |
| 13.10.7.1   | Operating Conditions                              | 2874 | 13.12.3     | High-Temperature Shift (HTS)                                  | 2906 |
| 13.10.7.2   | Processes for MTBE Production                     | 2875 | 13.12.3.1   | Fe—Cr Catalysts                                               | 2906 |
| 13.10.7.2.1 | Conventional MTBE Units                           | 2875 | 13.12.3.2   | Kinetics and Mechanism                                        | 2908 |
| 13.10.7.2.2 | Reactive Distillation in MTBE Production          | 2875 | 13.12.3.3   | Industrial Realization                                        | 2909 |
| 13.10.7.3   | Processes for ETBE Production                     | 2875 |             |                                                               |      |

- 13.12.3.4 Co–Cr Catalysts 2909
- 13.12.3.5 Chromium-Free Catalysts 2910
- 13.12.4 Low-Temperature Shift (LTS) 2910
  - 13.12.4.1 Copper Catalysts 2910
  - 13.12.4.2 Kinetics and Mechanism 2912
  - 13.12.4.3 Industrial Realization 2913
- 13.12.5 “Sour Gas” Shift 2914
  - 13.12.5.1 Molybdenum Catalysts 2914
  - 13.12.5.2 Kinetics and Mechanism 2914
  - 13.12.5.3 Industrial Realization 2914
- 13.12.6 COS Removal 2915
  - 13.12.6.1 Thermodynamics 2915
  - 13.12.6.2 Catalysts 2915
  - 13.12.6.3 Kinetics and Mechanism 2915
  - 13.12.6.4 Industrial Realization 2916
- 13.12.7 WGS over Supported Noble Metals 2916
  - 13.12.7.1 Platinum Catalysts 2916
  - 13.12.7.2 Gold Catalysts 2917
  - References 2918
- 13.13 Methanol Synthesis 2920
 

*John Bøgdil Hansen and Poul Erik Højlund Nielsen*

  - 13.13.1 Introduction 2920
  - 13.13.2 Thermodynamics 2920
  - 13.13.3 Methanol Synthesis Catalysts 2922
    - 13.13.3.1 Introduction 2922
    - 13.13.3.2 ZnO/Cr<sub>2</sub>O<sub>3</sub> Catalyst 2922
    - 13.13.3.3 Copper-Based Catalysts 2922
    - 13.13.3.4 Cu/ZnO + Element (Al, Cr, ...) 2922
    - 13.13.3.5 Promotion of Cu/ZnO/MOx Catalysts 2925
    - 13.13.3.6 Cu/ZrO<sub>2</sub> 2926
    - 13.13.3.7 Other Cu, Cu/Me, Cu/MeOx Catalysts 2926
    - 13.13.3.8 Pd-Based Catalysts 2927
    - 13.13.3.9 Sulfide Catalysts 2927
    - 13.13.3.10 Other Catalysts 2927
    - 13.13.3.11 Activation of Cu/Zn Catalyst 2928
    - 13.13.3.12 Activity as a Function of the Nature of Copper-Based Catalysts 2928
  - 13.13.4 Catalyst Deactivation 2929
    - 13.13.4.1 Sintering 2929
    - 13.13.4.2 Sulfur Poisoning 2930
    - 13.13.4.3 Other Poisons 2930
  - 13.13.5 By-Product Formation 2930
  - 13.13.6 Reaction Mechanism(s) and Active Sites 2931
    - 13.13.6.1 Cu<sup>+</sup> in a ZnO Matrix as the Active Center 2932
    - 13.13.6.2 The Schottky Junction Theory 2932
    - 13.13.6.3 Partly Oxidized Copper Independent of Support as Active Sites 2932
- 13.13.6.4 Metallic Copper in Dynamic Interaction with the Support 2933
- 13.13.6.5 Cu–Zinc Surface Alloy Model 2934
- 13.13.6.6 Water Gas Shift Reaction 2935
- 13.13.7 Kinetics 2935
  - 13.13.7.1 Reaction Rate Equations 2935
  - 13.13.7.2 Diffusion Restrictions 2937
  - 13.13.7.3 Kinetics in Slurry Phase Methanol Synthesis 2937
- 13.13.8 Methanol Synthesis Technology 2937
  - 13.13.8.1 Synthesis Gas Preparation 2937
  - 13.13.8.2 Natural Gas Reforming 2937
  - 13.13.8.3 Adiabatic Pre-Reforming 2937
  - 13.13.8.4 Tubular, Fired Reforming 2937
  - 13.13.8.5 Autothermal Reforming and Oxygen-Fired Secondary Reforming 2938
  - 13.13.8.6 Gasification of Heavy Oil, Coal or Biomass 2938
  - 13.13.8.7 Coproduction in Ammonia Plants and Use of Off-gases 2938
  - 13.13.8.8 Economics of Synthesis Gas Preparation 2938
  - 13.13.8.9 Reactor Systems and Synthesis Loop Layout 2939
  - 13.13.8.10 Slurry Phase Reactor Types 2940
  - 13.13.8.11 Methanol Purification 2941
  - 13.13.8.12 Concepts Circumventing the Equilibrium Limitations 2941
  - 13.13.8.13 Other Methanol Synthesis Routes and Technologies 2942
  - 13.13.8.14 Methanol Synthesis by Methane Activation 2942
- 13.13.9 Conclusion 2943
- References 2943
- 13.14 Methanol-to-Hydrocarbons 2950
 

*Steinar Kvisle, Terje Fuglerud, Stein Kolboe, Unni Olsbye, Karl Petter Lillerud, and Bipin V. Vora*

  - 13.14.1 Introduction 2950
  - 13.14.2 Industrial MTH Drivers 2950
    - 13.14.2.1 Monetization of Remote Natural Gas 2950
    - 13.14.2.2 Light Olefins: Supply and Demand 2950
    - 13.14.2.3 Methanol Technology 2951
  - 13.14.3 MTH Catalysis 2951
    - 13.14.3.1 Catalyst Systems 2952
    - 13.14.3.2 Reactions and Products 2952
    - 13.14.3.3 Catalyst System Properties and Modifications 2954
  - 13.14.4 Reaction Mechanisms 2955
    - 13.14.4.1 Carbene–Carbenoid Mechanisms 2955
    - 13.14.4.2 Carbocationic Mechanisms 2956
    - 13.14.4.3 Trimethyloxonium Intermediacy 2956

|             |                                                                                     |      |
|-------------|-------------------------------------------------------------------------------------|------|
| 13.14.4.4   | Radical Mechanisms                                                                  | 2956 |
| 13.14.4.5   | The Hydrocarbon Pool                                                                | 2956 |
| 13.14.4.5.1 | Product Formation                                                                   | 2956 |
| 13.14.4.5.2 | Parallel Reactions                                                                  | 2958 |
| 13.14.4.6   | Coke Formation                                                                      | 2958 |
| 13.14.5     | Reaction Kinetics                                                                   | 2958 |
| 13.14.6     | Reactor Technology                                                                  | 2959 |
| 13.14.7     | Process Descriptions                                                                | 2959 |
| 13.14.7.1   | UOP/Hydro MTO Process                                                               | 2959 |
| 13.14.7.2   | Integration of MTO with Olefin Cracking                                             | 2960 |
| 13.14.7.3   | Lurgi MTP <sup>®</sup> Process                                                      | 2960 |
| 13.14.7.4   | ExxonMobil MTO Technology                                                           | 2961 |
| 13.14.8     | Development and Commercial Status of the MTH Processes                              | 2961 |
| 13.14.8.1   | Mobil MTG                                                                           | 2961 |
| 13.14.8.2   | UOP/Hydro MTO Process                                                               | 2962 |
| 13.14.8.3   | Lurgi MTP <sup>®</sup> Process                                                      | 2962 |
| 13.14.8.4   | ExxonMobil                                                                          | 2962 |
| 13.14.9     | GTO Project Scenarios                                                               | 2962 |
| 13.14.10    | MTO and GTO Economics                                                               | 2962 |
| 13.14.11    | CO <sub>2</sub> Aspects                                                             | 2963 |
| 13.14.12    | Conclusions                                                                         | 2963 |
|             | References                                                                          | 2964 |
| 13.15       | The Fischer–Tropsch (FT) Synthesis Processes                                        | 2965 |
|             | <i>Mark E. Dry</i>                                                                  |      |
| 13.15.1     | Brief History                                                                       | 2965 |
| 13.15.2     | FT Synthesis as a Source of Fuels and Chemicals and its Viability                   | 2965 |
| 13.15.3     | Laboratory and Commercial FT Reactors                                               | 2966 |
| 13.15.4     | Commercial FT Plants                                                                | 2968 |
| 13.15.4.1   | Past and Present Plants (Post-1945)                                                 | 2968 |
| 13.15.4.1.1 | Brownsville, TX, USA                                                                | 2968 |
| 13.15.4.1.2 | Rentech, Pueblo, CO, USA                                                            | 2968 |
| 13.15.4.1.3 | Sasol, South Africa                                                                 | 2968 |
| 13.15.4.1.4 | PetroSA, South Africa                                                               | 2968 |
| 13.15.4.1.5 | Shell, Bintulu, Malaysia                                                            | 2969 |
| 13.15.4.2   | FT Plants Being Constructed or Planned                                              | 2969 |
| 13.15.4.2.1 | Qatar                                                                               | 2969 |
| 13.15.4.2.2 | Escravos, Nigeria                                                                   | 2969 |
| 13.15.4.2.3 | Exxon                                                                               | 2969 |
| 13.15.4.2.4 | Syntroleum                                                                          | 2969 |
| 13.15.4.3   | Other Activities in and Proposals for FT Operations                                 | 2969 |
| 13.15.5     | Catalysts for the Fischer–Tropsch Synthesis                                         | 2970 |
| 13.15.5.1   | Iron-Based Catalysts                                                                | 2970 |
| 13.15.5.1.1 | Catalysts for Wax Production                                                        | 2970 |
| 13.15.5.1.2 | Catalysts for the Production of Gasoline and Chemicals                              | 2971 |
| 13.15.5.1.3 | Alternative Iron-Based Catalysts                                                    | 2974 |
| 13.15.5.2   | Cobalt-Based Catalysts                                                              | 2974 |
| 13.15.5.2.1 | Cobalt Salts Used                                                                   | 2974 |
| 13.15.5.2.2 | Supports for Cobalt Catalysts                                                       | 2974 |
| 13.15.5.2.3 | Reduction and Promoters                                                             | 2975 |
| 13.15.5.3   | Catalysts Based on Metals Other than Iron or Cobalt                                 | 2975 |
| 13.15.5.4   | Deactivation of FT Catalysts                                                        | 2975 |
| 13.15.5.4.1 | Poisoning by Sulfur Compounds                                                       | 2976 |
| 13.15.5.4.2 | Deactivation of Iron Catalysts                                                      | 2976 |
| 13.15.5.4.3 | Deactivation of Cobalt Catalysts                                                    | 2977 |
| 13.15.6     | Kinetics of the Fischer–Tropsch Synthesis                                           | 2978 |
| 13.15.6.1   | Iron-Based Catalysts                                                                | 2978 |
| 13.15.6.2   | Cobalt-Based Catalysts                                                              | 2979 |
| 13.15.6.3   | Comparison of the Activity of Cobalt and Iron Catalysts                             | 2980 |
| 13.15.7     | FT Product Selectivities                                                            | 2981 |
| 13.15.7.1   | Primary and Secondary Reactions                                                     | 2981 |
| 13.15.7.2   | Product Distributions                                                               | 2983 |
| 13.15.7.3   | Control of Selectivity                                                              | 2984 |
| 13.15.7.3.1 | Temperature                                                                         | 2984 |
| 13.15.7.3.2 | Catalyst Metals and Promoters                                                       | 2984 |
| 13.15.7.3.3 | Gas Composition and Pressures                                                       | 2986 |
| 13.15.7.4   | Alcohol Production                                                                  | 2988 |
| 13.15.8     | Versatility of the FT Process and Product Quality Improvement                       | 2989 |
| 13.15.8.1   | Gasoline                                                                            | 2989 |
| 13.15.8.2   | Diesel Fuel                                                                         | 2990 |
| 13.15.8.3   | Chemicals                                                                           | 2990 |
| 13.15.9     | Possible Surface Reactions and Mechanisms                                           | 2990 |
| 13.15.9.1   | Development of Various Models                                                       | 2990 |
| 13.15.9.2   | Initial Reactions and Formation of Monomers                                         | 2991 |
| 13.15.9.3   | Possibility of Various Mechanisms Operating Simultaneously                          | 2991 |
| 13.15.9.4   | The Misfits of C <sub>1</sub> and C <sub>2</sub> Compounds in the ASF Distributions | 2991 |
| 13.15.10    | Environmental Aspects                                                               | 2991 |
|             | References                                                                          | 2992 |
| 13.16       | Gas-to-Liquids                                                                      | 2994 |
|             | <i>Tom J. Remans, Gregor Jenzer, and Arend Hoek</i>                                 |      |
| 13.16.1     | Introduction to GTL                                                                 | 2994 |
| 13.16.2     | Basic Steps in GTL                                                                  | 2995 |
| 13.16.3     | Synthesis Gas Production and Purification                                           | 2996 |
| 13.16.3.1   | Purification of Natural Gas                                                         | 2996 |

|             |                                                               |      |             |                                                               |      |
|-------------|---------------------------------------------------------------|------|-------------|---------------------------------------------------------------|------|
| 13.16.3.1.1 | Sulfur Removal                                                | 2997 | 13.17.3.2.1 | Distributed Oxygen Supply to a<br>Catalytic Fixed-Bed Reactor | 3017 |
| 13.16.3.1.2 | Hydrocarbon Removal                                           | 2998 | 13.17.3.2.2 | Counter-Current<br>Moving-Bed Reactor                         | 3018 |
| 13.16.3.1.3 | Trace Components Removal                                      | 2998 | 13.17.3.2.3 | Fluidized-Bed Reactors                                        | 3018 |
| 13.16.3.2   | Present Syngas Generation<br>Technologies                     | 2998 | 13.17.3.2.4 | Membrane Reactors                                             | 3019 |
| 13.16.3.2.1 | Non-catalytic Partial Oxidation<br>(POX)                      | 2999 | 13.17.3.3   | Process Concepts                                              | 3019 |
| 13.16.3.2.2 | Autothermal Reforming (ATR)                                   | 2999 | 13.17.4     | Conclusion                                                    | 3021 |
| 13.16.3.2.3 | Developments                                                  | 2999 |             | References                                                    | 3021 |
| 13.16.3.3   | Purification of Syngas                                        | 2999 | 13.18       | Catalysis in Direct Coal Liquefaction                         | 3023 |
| 13.16.4     | Fischer–Tropsch Reaction                                      | 3000 |             | <i>Matthias W. Haenel</i>                                     |      |
| 13.16.4.1   | Reactor Types                                                 | 3000 | 13.18.1     | Introduction                                                  | 3023 |
| 13.16.4.2   | Catalysts                                                     | 3000 | 13.18.2     | Coal Structure                                                | 3024 |
| 13.16.4.2.1 | Active Metals                                                 | 3001 | 13.18.2.1   | Organic Structure                                             | 3024 |
| 13.16.4.2.2 | Carriers                                                      | 3001 | 13.18.2.2   | Inorganic Structure                                           | 3026 |
| 13.16.4.2.3 | Promoters                                                     | 3002 | 13.18.2.3   | Physical Structure                                            | 3026 |
| 13.16.4.3   | Reaction Mechanisms and Kinetics                              | 3003 | 13.18.3     | Fundamental Transformations<br>in Direct Coal Liquefaction    | 3027 |
| 13.16.4.4   | Catalyst Poisons                                              | 3003 | 13.18.3.1   | Coal Properties                                               | 3027 |
| 13.16.4.4.1 | Sulfur Compounds                                              | 3003 | 13.18.3.2   | Primary Liquefaction Products                                 | 3028 |
| 13.16.4.4.2 | Others                                                        | 3004 | 13.18.3.3   | Solvent                                                       | 3028 |
| 13.16.5     | Mild Hydrocracking                                            | 3004 | 13.18.4     | Catalysis in Direct Coal Liquefaction                         | 3030 |
| 13.16.5.1   | Process Description                                           | 3004 | 13.18.4.1   | Dissolution Catalysts in the First<br>Liquefaction Stage      | 3030 |
| 13.16.5.2   | Catalysts                                                     | 3005 | 13.18.4.2   | Supported Catalysts                                           | 3032 |
| 13.16.5.2.1 | Composition                                                   | 3005 | 13.18.4.3   | Dissolved Catalysts                                           | 3033 |
| 13.16.5.2.2 | Other Requirements                                            | 3005 | 13.18.5     | Perspectives for Direct Coal<br>Liquefaction                  | 3033 |
| 13.16.5.2.3 | Reaction Mechanism                                            | 3006 |             | References                                                    | 3034 |
| 13.16.5.3   | Reactor                                                       | 3007 | 13.19       | Catalysis in Coal and Carbon<br>Gasification                  | 3037 |
| 13.16.6     | Products                                                      | 3007 |             | <i>Ljubisa R. Radovic</i>                                     |      |
| 13.16.6.1   | LPG                                                           | 3007 | 13.19.1     | Introduction                                                  | 3037 |
| 13.16.6.2   | Naphtha                                                       | 3007 | 13.19.2     | Processes                                                     | 3037 |
| 13.16.6.3   | Kerosene                                                      | 3007 | 13.19.3     | Catalysts                                                     | 3038 |
| 13.16.6.4   | Base Oils                                                     | 3007 | 13.19.4     | Mechanisms                                                    | 3041 |
| 13.16.6.5   | Gas Oil                                                       | 3007 | 13.19.5     | Conclusion                                                    | 3044 |
| 13.16.7     | Challenges in GTL, CTL and BTL                                | 3008 |             | References                                                    | 3044 |
|             | References                                                    | 3008 | 13.20       | Fuel Cell Related Catalysis                                   | 3045 |
| 13.17       | Oxidative Coupling of Methane                                 | 3010 | 13.20.1     | Fuel Processors                                               | 3045 |
|             | <i>Evgenii V. Kondratenko and Manfred Baerns</i>              |      |             | <i>Ralf Peters</i>                                            |      |
| 13.17.1     | Introduction                                                  | 3010 | 13.20.1.1   | Introduction                                                  | 3045 |
| 13.17.2     | Fundamentals of the OCM Reaction                              | 3010 | 13.20.1.2   | Energy Carriers for Fuel Cells                                | 3046 |
| 13.17.2.1   | Catalytic Materials and Their<br>Performance                  | 3010 | 13.20.1.3   | Thermodynamic Calculations                                    | 3048 |
| 13.17.2.2   | Mechanistic Aspects                                           | 3011 | 13.20.1.3.1 | Reforming Processes for Hydrogen<br>Production                | 3048 |
| 13.17.2.3   | Oxygen Species in the OCM<br>Reaction                         | 3013 | 13.20.1.3.2 | Thermodynamic Equilibrium<br>Calculations                     | 3049 |
| 13.17.2.4   | Structural Defects and Related<br>Physicochemical Properties  | 3014 |             |                                                               |      |
| 13.17.2.5   | New Approaches in Catalyst Design                             | 3016 |             |                                                               |      |
| 13.17.3     | Reaction and Process Engineering                              | 3017 |             |                                                               |      |
| 13.17.3.1   | Chemical Kinetics                                             | 3017 |             |                                                               |      |
| 13.17.3.2   | Modeling, Simulation and<br>Performance of Catalytic Reactors | 3017 |             |                                                               |      |

|             |                                                               |      |             |                                                                     |      |
|-------------|---------------------------------------------------------------|------|-------------|---------------------------------------------------------------------|------|
| 13.20.1.3.3 | Carbon Formation and Deposition                               | 3050 | 13.20.2     | Fuel Cells                                                          | 3081 |
| 13.20.1.4   | Fuel Pre-Processing                                           | 3053 |             | <i>Hubert A. Gasteiger and Jürgen Garche</i>                        |      |
| 13.20.1.4.1 | Removal of Harmful Species from Methanol and Water            | 3053 | 13.20.2.1   | Introduction                                                        | 3081 |
| 13.20.1.4.2 | Desulfurization                                               | 3053 | 13.20.2.2   | Working Principles of Fuel Cells                                    | 3081 |
| 13.20.1.4.3 | Evaporation of Liquid Fuels                                   | 3053 | 13.20.2.3   | Cell and Stack Construction                                         | 3082 |
| 13.20.1.5   | Methanol Steam Reforming                                      | 3054 | 13.20.2.3.1 | Alkaline Fuel Cells (AFCs)                                          | 3083 |
| 13.20.1.5.1 | Catalysts for Methanol Steam Reforming                        | 3054 | 13.20.2.3.2 | Proton Exchange Membrane Fuel Cell (PEMFC)                          | 3083 |
| 13.20.1.5.2 | Reaction Path of Methanol Steam Reforming on Cu/ZnO Catalysts | 3054 | 13.20.2.3.3 | Phosphoric Acid Fuel Cell (PAFC)                                    | 3085 |
| 13.20.1.5.3 | Active Sites of Cu/ZnO Catalysts                              | 3055 | 13.20.2.3.4 | Molten Carbonate Fuel Cell (MCFC)                                   | 3085 |
| 13.20.1.5.4 | Pd/ZnO Catalysts                                              | 3057 | 13.20.2.3.5 | Solid Oxide Fuel Cell (SOFC)                                        | 3086 |
| 13.20.1.5.5 | Kinetics of Methanol Steam Reforming                          | 3058 | 13.20.2.4   | Fuels for Fuel Cells                                                | 3087 |
| 13.20.1.5.6 | Reformer Design Based on Laboratory-Scale Experiments         | 3058 | 13.20.2.5   | Thermodynamics and Kinetics of Fuel Cells                           | 3088 |
| 13.20.1.5.7 | Example of Methanol Steam Reformer Development                | 3061 | 13.20.2.6   | Low-Temperature Fuel Cells with Gaseous Reactants                   | 3091 |
| 13.20.1.6   | Autothermal Reforming of Gasoline and Diesel                  | 3063 | 13.20.2.6.1 | Electro-Oxidation of Pure H <sub>2</sub>                            | 3092 |
| 13.20.1.7   | Internal Steam Reforming of Methane for SOFC Systems          | 3066 | 13.20.2.6.2 | Anodic H <sub>2</sub> Oxidation in the Presence of CO Contamination | 3094 |
| 13.20.1.8   | Gas Treatment for PEFC Systems                                | 3068 | 13.20.2.6.3 | Oxygen Reduction Reaction                                           | 3098 |
| 13.20.1.8.1 | Water-Gas Shift Reaction                                      | 3068 | 13.20.2.6.4 | Catalyst and Catalyst-Induced Degradation Mechanisms                | 3106 |
| 13.20.1.8.2 | CO Fine Cleaning                                              | 3069 | 13.20.2.7   | Fuel Cells for Direct Oxidation of Liquid Fuels                     | 3107 |
| 13.20.1.8.3 | Catalytic Combustion of Fuel Cell Tail Gases                  | 3072 | 13.20.2.7.1 | Direct Methanol Fuel Cells                                          | 3107 |
| 13.20.1.9   | Component and System Design                                   | 3073 | 13.20.2.7.2 | Direct Ethanol Fuel Cells                                           | 3113 |
| 13.20.1.9.1 | Heat Exchanger Networks                                       | 3073 | 13.20.2.7.3 | Direct Formic Acid Fuel Cells                                       | 3114 |
| 13.20.1.9.2 | Innovative Reactor Concepts                                   | 3074 | 13.20.2.8   | Fuel Cell Applications                                              | 3114 |
| 13.20.1.9.3 | Dynamic System Modeling                                       | 3074 | 13.20.2.8.1 | General                                                             | 3114 |
| 13.20.1.10  | Outlook                                                       | 3075 | 13.20.2.8.2 | Transportation Applications                                         | 3115 |
|             | References                                                    | 3076 | 13.20.2.8.3 | Stationary Application                                              | 3115 |
|             |                                                               |      | 13.20.2.8.4 | Portable Applications                                               | 3116 |
|             |                                                               |      | 13.20.2.9   | Final Comments                                                      | 3116 |
|             |                                                               |      |             | References                                                          | 3117 |