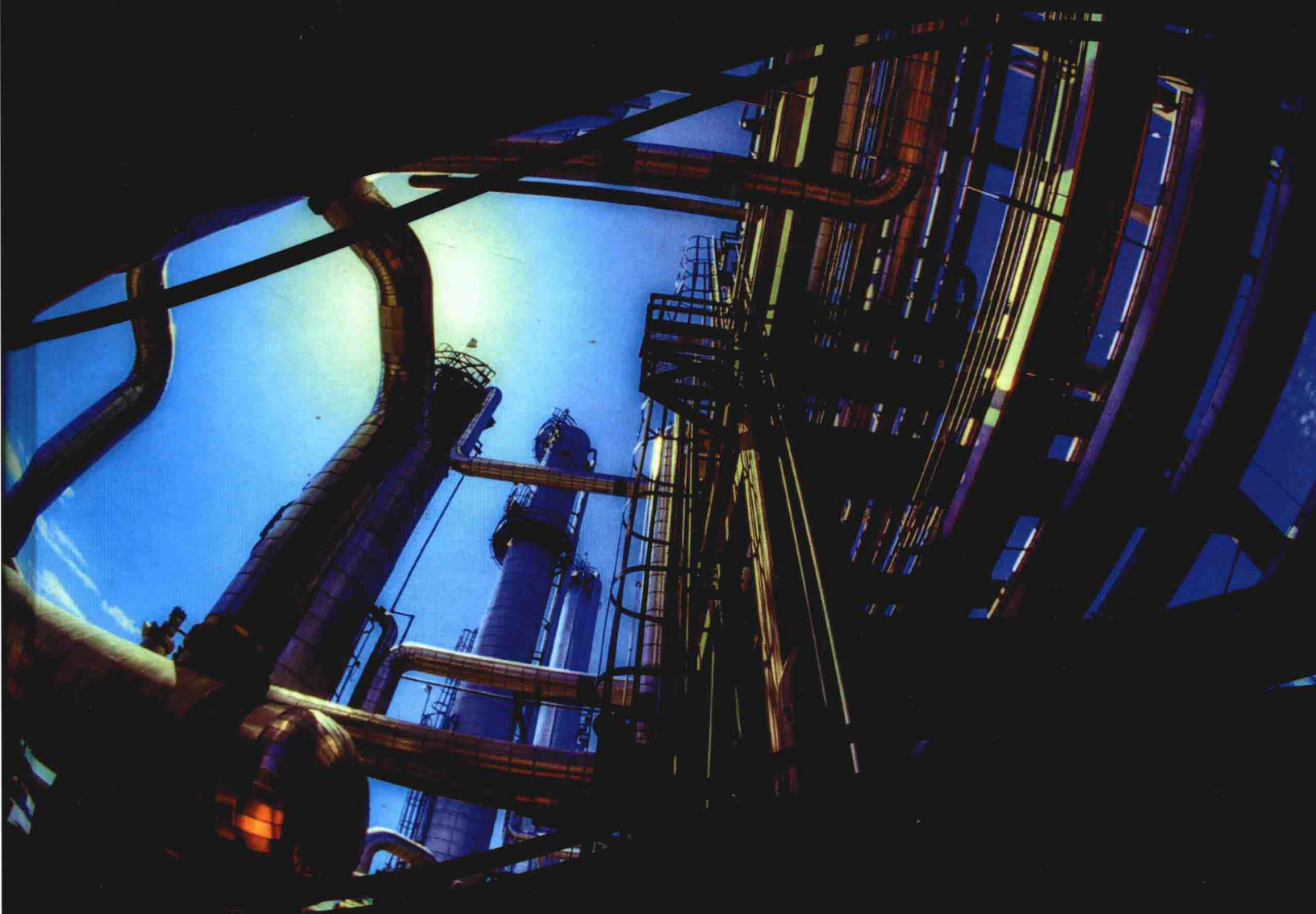


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# Petrochemical Catalyst Materials, Processes, and Emerging Technologies



Hamid Al-Megren and Tiancun Xiao



# Petrochemical Catalyst Materials, Processes, and Emerging Technologies

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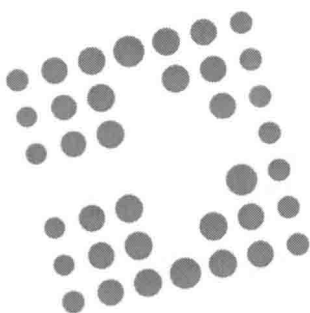
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*Kathryn R. Williams, University of Florida, USA*

*Kenneth Boone Wagener, University of Florida, USA*

The use of acyclic diene metathesis (ADMET) in the synthesis of functionalized polyolefins is discussed. The nature of polymerizations, catalysts, and techniques are briefly covered. An overview of recent functionalized ADMET polymers and major contributions to its methodology is given. This chapter will place special emphasis on the use of ADMET to synthesize increasingly complex and new morphologies, resulting in well-defined polyolefin structures and functionalized materials unlocked as a result of this powerful polymerization method. Presented are polyolefins, materials, and architectures not possible through conventional polymerization techniques.

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*Srikant Gopal, SABIC Technology Center, Saudi Arabia*

*Mohammed H Al-Hazmi, SABIC Technology Center, Saudi Arabia*

The main challenge for selective oxidation catalysis has always been achieving an economically viable selectivity. In this chapter, the advances made around the last decade in catalyst development for the selective oxidation of C2-C4 alkanes to carboxylic acids and olefins are discussed. To assess the progress made and to study the trends, particular attention has been given to the results reported in patents. A review of the developments reported in the research literature and new knowledge about the catalysts and their functioning have also been summarized. A comparison with existing processes is provided to obtain an idea of which selective oxidation routes are approaching closer to commercial implementation. Finally, some of the challenges that the selective oxidation routes must overcome for widespread commercial adoption are discussed and suggestions for future research are provided.

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*Venkata Narayana Kalevaru, Leibniz-Institute for Catalysis, Germany*

*Jörg Radnik, Leibniz-Institute for Catalysis, Germany*

Palladium is one of the precious group metals mainly used in automobile catalytic converters. Besides, it has an importance in various catalytic processes. Although it is well known for hydrogenation reactions, various oxidations can also be catalyzed by palladium. This chapter gives an overview on the most common application of palladium catalysts in heterogeneously catalyzed acetoxylation, i.e. the acetoxylation of ethylene to vinyl acetate. Derived from this knowledge, the authors summarize in detail recently accumulated research results in acetoxylation of toluene to benzyl acetate that can be easily converted to benzyl alcohol. The chapter includes a detailed description of catalyst syntheses, gas phase oxidation runs, comprehensive characterizations and a deep understanding in catalyst-feed interaction. This development can turn away the manufacture of important petrochemicals from chlorine chemistry to oxidations using molecular oxygen.

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*Abdulaziz Bagabas, King Abdulaziz City for Science and Technology, Saudi Arabia*

*Andreas Martin, Leibniz Institute for Catalysis, Germany*

Ethylene is the largest of the olefin markets and is also one of the most important petrochemically derived monomers that are used as a feedstock for the production of various commercially useful chemical products (e.g. polyethylene, polymers, fibers etc.). The primary objective of this chapter is to provide a comprehensive overview about olefins particularly ethylene production technologies and its commercial significance in the world market. The content of this chapter is presented as follows: a general overview about olefins production is given. This is followed by introducing the reader to ethylene including its properties importance/applications. The next section describes the production technologies of ethylene and some of its selected derivatives, followed by an overview of the technology, market, costs, capacity, global demand and supply of ethylene technology. Finally, main points and outlook of this highly industrially important commodity chemical are summarized.

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Nowadays, an important contribution to the sustainable industrial growth might come not only from the development of new materials but also from the re-design of process engineering, which leads to the development and the re-designing of more compact and efficient new processes in many areas of applications. As already done in large part of processes in Nature, membrane operations can serve in molecular separations, chemical transformations, water and energy transfer between different phases.



Indeed, these technologies well fit the principles of this design philosophy and this is testified by the various applications of membranes in chemical and petrochemical industry and many are the successful examples of processes that have moved from lab-scale to pilot plant up to a demonstration unit in refinery. The main aim of this chapter is to show the main applications of membrane technology in the petrochemical industry and the related current research trends, focusing on the impact that membrane technology can have on the process sustainability.

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*Hisham S Bamufleh, King Abdulaziz University, Saudi Arabia*

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*Mahmoud M. El-Halwagi, Texas A&M University, USA*

The petrochemical industry has a substantial impact on the environment through the use of large quantities of natural resources (mass and energy) and discharge of wastes into the environment. Process integration offers a powerful framework for the sustainable development of the petrochemical through conservation of mass and energy and synergism among the different building blocks in the supply chain. The chapter provides an overview of process integration basics and tools that can be used to enhance the performance of the petrochemical industry. The chapter also describes the key building blocks of the petrochemical supply chain and how they may be integrated. Finally, the chapter describes key drivers and opportunities of process integration within individual petrochemical plants, among various petrochemical facilities, and the relationship to the existing refining infrastructure.

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*Ravinder Singh, Lamar University, USA*

*Helen Huiru Lou, Lamar University, USA*

Liquefaction of natural gas helps in transporting it over long distances by sea vessels. It is then regasified and transported through pipelines to the consumer. Due to large energy density of Liquefied Natural Gas (LNG), and associated flammability issues, the LNG terminal involves high risk. Consequently, safety is an important factor in the operation of LNG terminals. Although a substantial amount of time money and effort has been put in this area, there is always some possibility of improving the process so that less risk is involved. Rapid advancement in process simulation software like Aspen Plus and Aspen HYSYS, has led to the convenience of experimenting the various control methodologies on the computer offline from the actual plant operation, before they are implemented in real time. In this chapter, main hazards associated with LNG terminal operation will be highlighted. Further, recent advancements in research for safety enhancement and efficiency enhancement in the liquefaction and regasification processes will also be included.



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*Jie Sun, Xiamen University, China*

*Shaolong Wan, Xiamen University, China*

*Jingdong Lin, Xiamen University, China*

*Yong Wang, Pacific Northwest National Laboratory, USA*

Ethanol and higher alcohols (C<sub>2</sub>+OH) have attracted much attention owing to their wide applications. They can be produced from syngas using homogeneous and heterogeneous catalysts. Although homogeneous catalysts exhibit high productivity and selectivity of C<sub>2</sub>+OH, difficulties in separating and recycling homogeneous catalysts remain challenging. Among heterogeneous catalysts, Rh-based catalysts show promising higher selectivity of C<sub>2</sub>+OH. However, prohibitive cost of Rh metal hinders its large-scale application. Non-noble metal based heterogeneous catalysts include modified methanol synthesis catalysts, modified Fischer-Tropsch (F-T) synthesis catalysts, and Mo/MoS<sub>2</sub>-based catalysts. Compared with the modified F-T synthesis catalysts and Mo/MoS<sub>2</sub>-based catalysts, production of undesired byproducts on modified Cu-based catalysts can be well suppressed. Here, the influences of additives and supports on catalytic activity of modified Cu-based catalysts are discussed. Reaction mechanism and development of novel reactors are also included.

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In this work, a series of supported CoMo or NiMo HDS catalysts have been prepared based on the organic-metal matrix decomposition method and tested for diesel deep HDS with minimum hydrogen consumption under relatively low hydrogen partial pressure conditions. The aim is to develop a HDS catalyst which can reduce sulphur in diesel fuel from 5000ppm down to 50 ppm in a single pass with minimum hydrogen consumption under the conditions of 340°C, 35 bar, LHSV 1.2 h<sup>-1</sup> with low H<sub>2</sub>/oil ratio. The catalysts preparation process was monitored and the resultant catalyst samples before and after the HDS performance test have been characterised, some interesting results have been obtained. The presence of citric acid as organic additive/dispersing agent/chelating agent in the impregnation solution improved HDS activity compared to the equivalent CoMo catalyst prepared without citric acid. The order of activity of the cobalt precursors is Co citrate > Co acetate > Co nitrate.

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*Tauqeer Abbas, COMSATS Institute of Information Technology, Pakistan*

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*Xiaochun Chen, Beijing University of Chemical Technology, China*

Hydrodesulphurization (HDS) is a standard process for removing sulphur compounds in fuel oils in industry. HDS is effective to remove simple aliphatic sulphur compounds while less effective to remove thiophenes, dibenzothiophenes, and their derivatives because of sterically hindered adsorption on catalyst surface. Application of ionic liquids (ILs, a new class of compounds) substituting for traditional volatile organic solvents in extractive desulphurization (EDS) or oxidative desulphurization (ODS), have been being studied intensively in the latest decades, and many very promising results have been obtained, showing a good prospect as complement method to HDS. In this chapter, these fresh research results of EDS and ODS using ILs are summarized along with comprehensive discussions on diversified desulphurization factors along with some potential problems. It can be inferred that ILs are a class of potential ideal solvents to realize clean fuel oil in future although some problems come too.

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*Youquan Deng, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China*

*Shimin Liu, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China*

There has been still a growing interest in ionic liquids (ILs) for catalysis, in particular considering their tremendous success made over the past decades. Indeed, ILs for catalysis has been a main subject in chemistry and technology, and a rough estimate is that more than 6000 publications involving IL catalysis have been reported in the past fifteen years. Since there have been a large number of excellent reviews and books concerning the catalysis in ILs, in this chapter the authors mainly focus on the IL immobilized nano- or super-fine metal particles for catalysis, which could bridge or fill the gap between homogeneous and heterogeneous catalysis. Detailed IL-immobilized catalyst preparation, characterization and their application in hydrogenation, C-C coupling, oxidation, etc. will be discussed.

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*Masahiro Kishida, Kyushu University, Japan*

Kinetic models were developed to account for the partial contributions of intermediates in complex parallel-consecutive reactions. The models allow precise estimation of the apparent rate constants of all steps in such a reaction network. The hydrodesulfurization (HDS) of dibenzothiophene (DBT) over CoMo-based alumina and carbon catalysts, and over an unsupported molybdenum sulfide catalyst, were investigated in a batch reactor and used to represent this type of reaction. The HDS reactions proceeded

through two parallel–consecutive reaction pathways, i.e., direct desulfurization (DDS) and hydrogenation (HYD), in which two main intermediates, namely biphenyl and partially hydrogenated DBT, were involved. Different selectivities in terms of yield fraction (percentage ratio of HYD/DDS) were observed for these catalysts. The results are discussed in the context of proposed HDS reaction networks. Use of these models enables more accurate assessment of differences among the performances of different catalysts.

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*Ceri Hammond, Cardiff University, UK*

*Laura Prati, Università degli Studi di Milano, Italy*

The selective transformation of biomass-derived compounds to useful fine chemicals and fuels has developed rapidly in recent years, and biomass compounds will soon become one of the main resource contributors for the production of chemicals. In the near future, it is expected that biomass derived compounds will contribute substantially to global chemical production along with fossil-based analogues. Although, there is still debate about the sustainability of the usage of biomass-derived molecules, it is important to emphasise that effort has been made to use biomass in the most efficient way, and that the biomass resources used are not suitable for food purposes. In this review we will focus to present selected examples on the transformation of glycerol in three distinct areas; (i) glycerol oxidation, (ii) glycerol hydrogenolysis and (iii) glycerol aqueous reforming, using supported metal nanoparticles as the chosen catalysts.

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*Serbia M. Rodulfo-Baechler, University of Newcastle, UK*

The Mixed Ionic and Electronic Conducting (MIEC) membrane reactors are of interest because they have the potential to produce high purity oxygen from air at lower costs and provide a continuous oxygen supply to reactions or/and industrial processes. The study of the dual role oxygen flux and catalytic performance of the unmodified and Ni-coated  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  hollow fibre membranes (LSCF6428 HFM) in the methane oxidation reactions (i.e., partial oxidation of methane and methane combustion) by using air on lumen side and methane on shell side are shown in this chapter. The LSCF6428 HFM participates not only in the oxygen flux but also in the methane conversion to  $\text{C}_2$ . A Ni-coated LSCF6428 HFM under lean  $\text{O}_2/\text{CH}_4$  gradient (i.e., 0.5) showed the production of syngas, carbon dioxide and  $\text{C}_2$  products in agreement with the thermodynamic calculation. At rich  $\text{O}_2/\text{CH}_4$  gradient (i.e., 1.0), the formation of carbon dioxide was facilitated. The main catalytic pathway at lean  $\text{O}_2/\text{CH}_4$  gradient and  $\text{H}_2$  reduction treatment was partial oxidation of methane to  $\text{C}_2$  and syngas.

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*Pingyi Wu, Beijing University of Chemical Technology, China*

*Ling Lan, PetroChina, China*

*Shengfu Ji, Beijing University of Chemical Technology, China*

Hydrodesulfurization (HDS) is an important technology to produce clean fuels, in which the nickel phosphide catalysts exhibit excellent catalytic performances. In this work, a series of Ni<sub>x</sub>P/SBA-15 catalysts with various P/Ni molar ratios were prepared using the mesoporous molecular sieve SBA-15 as the support. The structure and surface properties of the catalysts were characterized by X-ray diffraction (XRD), N<sub>2</sub> sorption analysis, transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FTIR), and in situ diffuse reflectance infrared Fourier transfer spectroscopy (DRIFTS). The catalytic performances for the HDS of dibenzothiophene (DBT) were evaluated. The results demonstrated that the Ni<sub>x</sub>P/SBA-15 catalysts possessed high specific surface area and the mesoporous structures, which benefited the elimination of the internal diffusion limitation in the HDS reactions. Both Ni<sub>2</sub>P and Ni<sub>12</sub>P<sub>5</sub> phases showed catalytic activity in HDS reactions while Ni<sub>2</sub>P was more active. The optimal P/Ni molar ratio was about 0.75. The DBT conversion can reach 95.8% under the reaction condition of pressure at 3.0 MPa, H<sub>2</sub>:oil=600, WHSV at 26.7 h<sup>-1</sup>, and temperature at 340°C. In situ DRIFTS spectra indicated that the coordinative unsaturated Ni<sup>δ+</sup> (0<δ<1) species on the catalysts surface were the active sites for the HDS of DBT.

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## Preface

Dear Readers,

It is our great honor to present this IGI Global Series book on the “Petrochemical Catalyst Materials, Processes, and Emerging Technologies”. As we know that Petrochemical Industry is a technology-intensive sector, where any small changes in the technology could lead to a big improvement. The development and understanding of chemical processes relies on knowledge of various disciplines, from raw materials, reaction mechanism, process parameters and the target materials. In the modern information age, lots of changes are happening every day in petrochemical industry, such as new materials discovery and application, process modification and automation, market and demand changes, thus leading to new and emerging technologies.

This IGI Global book is to address the latest development in the petrochemical technologies, especially focusing on the core technologies such as catalyst materials for fuel upgrading, especially on sulfur removal, syngas conversion, alkane and oxygen activation, functionization of polymer. Of course safety is always the top priority in petrochemical industry, so we also cover these topics for the expanding LNG industry. The chapters cover research from mechanism study to the industry catalysts development, from homogenous catalysis to the heterogeneous catalyst and from small molecules activation to the heavy oil upgrading. This book also includes both the conventional process like supported catalysts, and latest catalytic process and materials in ionic liquid, the chemicals resources include fossil fuel, syngas as well as the glycerol, the renewable resources. These will be helpful for the academic researchers and the industrial engineers for them to have a quick view on the latest development in these areas.

Compilation of a professional book is a trivial job, which takes us 15 months. However, we are encouraged by the very enthusiastic authors from various countries, they actively responded for the call for chapters and we initially have received more than 50 plans for chapters. We screened down to 26 chapters for full writing, and after submission and extensive reviewing, we are very pleased to include 15 chapters in this book.

Here we would like to express our sincere thanks to these contributors for their hard and serious working, also we like to thanks our reviewers for their constructive input. Last but not least, thanks are due to IGI Global for giving us the chance to edit the book. We hope readers would enjoy the reading and feel free to point any errors or mistakes which we may not be spotted. Your comments and suggestions are highly appreciated.

Yours sincerely,

*Hamid Al-Megren*

*King Abdulaziz City for Science and Technology, Saudi Arabia*

*Tiancun Xiao*

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