

FUEL CELLS:

TECHNOLOGIES FOR FUEL PROCESSING



EDITED BY
D. SHEKHAWAT, J.J. SPIVEY, AND D.A. BERRY

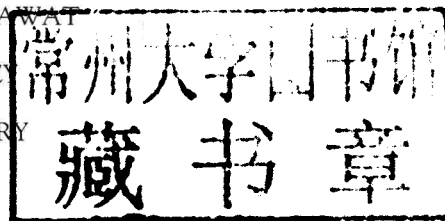
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DUSHYANT SHEKHAVAT

JAMES J. SPIVEY

DAVID A. BERRY



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FUEL CELLS: TECHNOLOGIES FOR FUEL PROCESSING

Preface

FUEL CELLS: TECHNOLOGIES FOR FUEL PROCESSING

Fuel cells are rapidly approaching commercial viability. Fuel cells are clean and efficient energy sources for transportation, stationary, and distributed power. Private industry, academia, as well as government agencies (particularly in developed countries) are actively engaged in developing cost effective fuel cell technology. The fuel processor is a critical component of a fuel cell power system and must be able to provide a clean H₂ or H₂-rich synthesis gas to the fuel cell stack for long-term operation. In spite of the increasing technical and commercial importance of fuel cells, there are few books in which fuel processing technology is treated comprehensively. The majority of books over the years about fuel cells address fuel processing technologies only briefly; e.g., in a single section in a chapter.

Fuel Cells: Technologies for Fuel Processing provides an overview of the most important aspects of fuel reforming to the generally interested reader, researcher, technologist, teacher, student, or engineer. The topics covered include all aspects of fuel reforming: fundamental chemistry, different modes of reforming, catalysts, catalyst deactivation, fuel desulfurization, reaction engineering, novel reforming concepts, thermodynamics, heat and mass transfer issues, system design, and recent research and development.

By focusing on the fundamentals, this book is intended to be a source of information now and in the future. By avoiding time-sensitive information/analysis (e.g., economics) this book will serve as a single source of information for scientists and engineers in fuel processing technology. The material is presented in such a way that this book will serve as a reference for graduate level courses, fuel cell developers, and fuel cell researchers.

No attempt is made to describe the fuel cell itself—e.g., there is no in-depth discussion of the various electrolytes in proton exchange membrane (PEM) or solid oxide fuel cells (SOFCs). Rather, a sufficient description of the fuel cell is included to show how it affects the fuel reformer—e.g., CO removal from the reformat is required by PEMs, but not SOFCs. Also, no attempt was made to include the hydrogen production from non-carbon sources such as water electrolysis, borohydrides, etc.

It is a pleasure to thank those who have made this project possible. First of all, we would like to thank all our coauthors. We are very grateful they were able to dedicate their valuable time to this project. It has been our pleasure to work with all the contributors involved in this book. Their effort in combining their own research with recent literature in the field of fuel processing is highly appreciated. This effort would not have been possible without their willingness to share their valuable knowledge, insight, and experience. Moreover, we express our gratitude

for their responsiveness to deadlines and review comments.

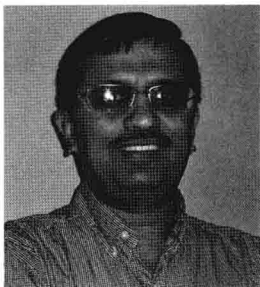
We also want to express our sincere gratitude to all reviewers who provided their thoughtful and timely comments. We would like to thank Debra Benson (Performance Results Corporation, Morgantown, WV) for her skillful assistance in modifying and redrawing several figures for this book. We would like to thank Stacy Kief (U.S. Department of Energy, Morgantown, WV) for authentication of the text. We gratefully acknowledge Mark W Smith (URS Corporation, Morgantown, WV) for his kind suggestions throughout this project. Thanks to Mike

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Dushyant Shekhawat
James J. Spivey
David A. Berry

Editors Biography

Dushyant Shekhawat



Dushyant Shekhawat is a researcher at National Energy Technology Laboratory (U.S. Department of Energy), Morgantown, WV, USA. He received his BS in Chemical Engineering from the University of Minnesota in Twin Cities and his PhD in Chemical Engineering from the Michigan State University in East Lansing. His research interests include: fuel processing for fuel cell applications, reaction engineering, surface chemistry, heterogeneous catalysis, energy, fuel cell, plasma and radio frequency- assisted fuel reforming, and plasma chemistry. He has served as a guest-editor for the special issues of *Catalysis Today* (Reforming of Liquid Hydrocarbon Fuels for Fuel Cell Application) and the journal of *Fuel* (Advanced Fossil Energy Utilization). Shekhawat is a registered Professional Engineer (PE) in West Virginia and also serves on the NCEES's PE Chemical Engineering Exam Committee,

which produces the Professional Engineer Examination for chemical engineers. He is a member of the American Chemical Society and American Institute of Chemical Engineers.

David A. Berry



David A. Berry is Director of the Separations and Fuel Processing Division at the Department of Energy's National Energy Technology Laboratory (NETL). He has 24 years of extensive experience in energy-related research & development programs involving coal, oil, and natural gas. His research career has spanned fundamental through system-level development most specifically related to fuel cell, turbine and gasification technologies. His current focus is on CO₂ capture research and development of catalytic oxidation and syngas conversion processes. He has served on the Editorial Board for *Catalysis Today*.

James J. Spivey

James J. Spivey is the Shivers Professor of Chemical Engineering at Louisiana State University (LSU). He received his BS and MS

at North Carolina State University, and his PhD from LSU. He currently serves as Director of the Center for Atomic-level Catalyst Design, a U.S. Dept. of Energy-funded Center focusing on developing new computational, synthesis, and characterization tools for heterogeneous catalysts. His research career has been directed toward the application of fundamental catalysis to problems such as clean energy, conversion of syngas to higher value products, environmental catalysis, and activation of CO₂ and methane. He is the Editor-in-Chief of *Catalysis Today*, and Editor of the *Catalysis* book series published by the Royal Society of Chemistry (Cambridge, UK), and is also a Fellow of the Royal Society of Chemistry.

Contributors

- Ahmet K. Avci** Department of Chemical Engineering, Boğaziçi University, Bebek 34342, Istanbul, Turkey, Phone: +90-212-3597785, Email: avciahme@boun.edu.tr
- David A. Berry** National Energy Technology Laboratory, U. S. Department of Energy, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA, Phone: +1-304-285-4430, Email: david.berry@netl.doe.gov
- Robert A. Dagle** Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA, Phone: +1-509-375-6264, Email: robert.dagle@pnl.gov
- Alexander Fridman** A.J. Drexel Plasma Institute, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA, Phone: +1-215-895-1542, Email: af55@drexel.edu
- Michael J. Gallagher** URS Corporation, National Energy Technology Laboratory, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA, Phone: +1-304-285-4835, Email: michael.gallagher@ur.netl.doe.gov
- Santosh K Gangwal** Southern Research Institute - North Carolina, Advanced Energy and Transportation Technologies, 5201 International Drive, Durham, NC 27712, USA, Phone: +1-919-282-1053, Email: gangwal@southernresearch.org
- Jing Gao** Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou, 310028, China, Phone: +86-571-88273283, Email: pinkjinggao@163.com
- John B. Hansen** Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark, Phone: +45-4527-2459, Email: jbh@topsoe.dk
- Daniel J. Haynes** National Energy Technology Laboratory, U. S. Department of Energy, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA, Phone: +1-304-285-1355, Email: daniel.haynes@netl.doe.gov
- Zhaoyin Hou** Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou, 310028, China, Phone: +86-571-885103987, Email: zyhou@zju.edu.cn
- Ayman M. Karim** Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA, Phone: +1-509 375-4186, Email: ayman.karim@pnl.gov
- David L. King** Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA, Phone: +1-509-375-3908, Email: david.king@pnl.gov
- Guosheng Li** Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA, Phone: +1-509-371-6520, Email: guosheng.li@pnl.gov
- Hui Lou** Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou, 310028, China, Phone: +86-571-88273283, Email: louhui@tom.com
- Rich Mastanduno** Precision Combustion, Inc., 410 Sackett Point Road, North Haven, CT 06473, USA, Phone: +1-203-287-3700 x264, Email: rmastanduno@precision-combustion.com
- Jens R. Rostrup-Nielsen** Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark, Phone: +45-4527-2397, Email: jrn@topsoe.dk
- Z. Ilsen Önsan** Department of Chemical Engineering, Boğaziçi University, Bebek 34342, Istanbul, Turkey, Phone: +90-212-3596412, Email: onsan@boun.edu.tr
- Subir Roychoudhury** Precision Combustion, Inc., 410 Sackett Point Road, North Haven, CT 06473, USA, Phone: +1-203-287-3700 x267, Email: sroychoudhury@precision-combustion.com
- Dushyant Shekhawat** National Energy Technology Laboratory, U. S. Department of Energy, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA, Phone: +1-304-285-4634, Email: dushyant.shekhawat@netl.doe.gov

Mark W. Smith URS Corporation, National Energy Technology Laboratory, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA, Phone: +1-304-285-4126, Email: mark.smith@netl.doe.gov

James G. Speight CD & W Inc., 2476 Overland Rd, Laramie, WY 82070, USA, Email: jamesp8@aol.com

James J. (Jerry) Spivey Gordon A. and Mary Cain Department of Chemical Engineering, Louisiana State University, S. Stadium Drive, Baton Rouge, LA 70803, USA, Phone: +1-225-578-3690, Email: jjspivey@lsu.edu

Yu Su Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

Mark C. Williams URS Corporation, National Energy Technology Laboratory, 3610 Collins Ferry Rd, Morgantown, WV 26507, USA, Phone: +1-304-285-4344, Email: mark.williams@ur.netl.doe.gov

Xiaoming Zheng Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou, 310028, China, Phone: +86-571-88273283, Email: xmzheng@dial.zju.edu.cn

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Introduction to Fuel Processing

*Dushyant Shekhawat**, *David A. Berry**, *James J. Spivey*†

*National Energy Technology Laboratory, U.S. Department of Energy, 3610 Collins Ferry Road, Morgantown, WV 26507-0880, USA and †Department of Chemical Engineering, Stadium Drive, Louisiana State University, Baton Rouge, LA 70803, USA

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1.1. CLEAN ENERGY

One of the most critical challenges facing the world is the development of clean, reliable, and efficient energy conversion processes. Because the standard of living of virtually all nations is directly related to per capita energy consumption [1,2], the demand for energy will inevitably increase. At the same time, it is widely accepted that this increasing demand for energy must not compromise the environment.

Advanced technologies designed to meet this challenge include processes as different as

wind, solar, hydroelectric, photovoltaic, and others. Among the most promising near-term technologies are those based on fuel cells, which convert chemical energy into electrical energy with higher efficiencies and far fewer environmental effects than other options. Several studies have recently reported on the technical viability and economics of fuel cell systems for various applications [3–14]. Fuel cells are being developed for use in transportation as well as for stationary and distributed power systems.

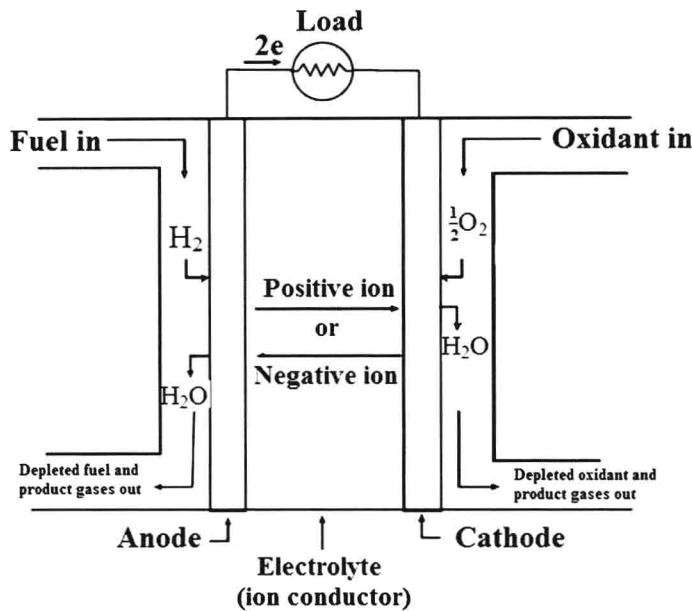


FIGURE 1.1 Schematic representation of an individual fuel cell [15].

1.2. FUEL CELLS

Fuel cells are essentially continuously operating batteries, which generate electricity from a fuel, such as hydrogen, and an oxidant, such as air. A schematic representation of a fuel cell with the product/reactant gases and the ion conduction flow directions through the cell is shown in Fig. 1.1.

Each type of fuel cell is designed to meet a different application. For example, the proton exchange membrane (PEM) fuel cell is being pursued by a number of companies because of its low operating temperature, response to transients [16], and compact size, which make it desirable for a number of residential [17–20], commercial, and military [21] applications. Solid oxide fuel cells (SOFCs) are being developed for small-scale stationary power applications, auxiliary power units (APUs) for vehicles [8,22–24], mobile generators for civilian as well as military applications [25]. See Chapter 2 for a detailed discussion of various fuel cells and their specific applications.

1.3. FUEL PROCESSORS

The purpose of a fuel processor is to convert a commonly available fuel, such as gasoline, diesel, or natural gas, into a gas stream containing primarily, or only, the compound(s) required by the fuel cell. A representative process diagram for a fuel processor designed to convert a liquid fuel (with added water to maximize H_2 yield and prevent catalysts

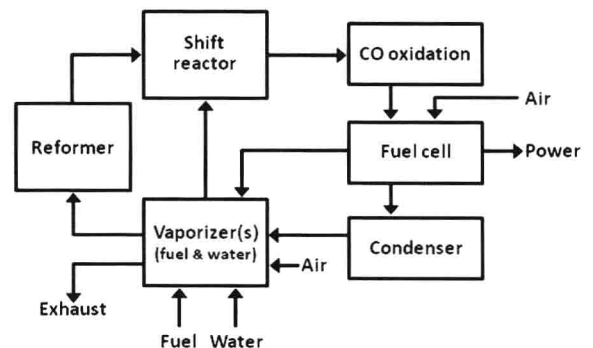


FIGURE 1.2 Generic fuel processor.

deactivation) into a CO-free gas stream containing essentially only H₂ and CO₂ is shown in Fig. 1.2. The fuel processor may consist of three steps, depending on the type of fuel cell (high or low temperature) it is coupled with: reforming of the liquid fuel into syngas, water gas shift (WGS), and preferential oxidation of CO.¹

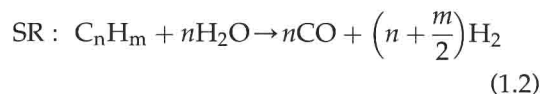
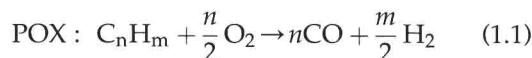
The fuel to power the fuel cells can, in principle, be a wide range of oxidizable compounds, such as hydrogen, CO, CH₄, and methanol. Regardless of the type of fuel cell, the fuel processor must produce a hydrogen-rich gas stream. Because a widely available hydrogen infrastructure does not exist, the hydrogen-rich gas can most readily be derived from the reforming of hydrocarbon fuels, which can take advantage of a well-developed existing infrastructure. Depending on the application, there are a wide range of conventional fuels, such as natural gas (methane) [26,27], methanol [28,29], ethanol [30,31], dimethyl ether [32,33], propane [34,35], butane [36,37], gasoline [38,39], kerosene [40,41], jet fuels [24,42], diesel [43,44], and biodiesel [45,46], which can be reformed to produce the hydrogen-rich reformat needed to power the fuel cell. Alcohol-based fuels are also widely studied for the production of H₂ for fuel cells because they can be reformed at relatively low temperatures and are free of sulfur compounds. Fischer–Tropsch fuels, which

contain virtually no sulfur, aromatics, metals, or other toxics [47], are also being considered for reforming applications.

Because each type of fuel cell requires a different fuel, the fuel processor must be designed to match the fuel cell. For example, low-temperature fuel cells like PEMs require relatively pure hydrogen and cannot operate in the presence of CO concentrations greater than 10–20 ppm for any significant time. However, high-temperature fuel cells like SOFCs can utilize CO as well as hydrogen, so the shift reactor and CO oxidation step would not be needed, and reformat could be fed directly to the fuel cell.

1.4. REFORMING MODES

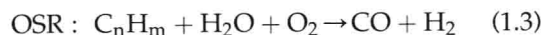
There are three predominant modes of catalytic reforming: partial oxidation (POX), steam reforming (SR), and oxidative steam reforming (OSR).² All three involve oxidation of the hydrocarbon fuel to produce a hydrogen-rich synthesis gas. These three reactions are shown below³:



¹ In this configuration, water is added to maximize H₂ yield and to minimize catalyst deactivation. Water is not essential, but illustrates one design option. Also note that the fuel cell exhaust, consisting primarily of steam and CO₂, is condensed and (at least partially) recycled in this example. This can help maximize overall thermodynamic efficiency. A separate gas cleanup step, which would typically be located just downstream of the reformer, is not shown, but may be needed in some applications.

² Autothermal reforming (ATR) is a special case of OSR, in which the ratio of oxygen and steam is such that the net heat of reaction is zero at the reformer temperature.

³ These reactions show only CO and H₂ as the products. CO₂ and H₂O are inevitably present in the product gas as well, but are not shown here for the sake of simplicity since CO and H₂ are the oxidizable products of the reforming reactions, and hence the fuels of interest for fuel cell applications. Note that the stoichiometry of the OSR reaction is not unique - there is no unique set of stoichiometric coefficients that balance the equation. See note 2 - ATR corresponds to one set of coefficients that both balances the equation and results in a net heat of reaction of zero at the reformer temperature.



The mode of operation has a significant impact on overall efficiency and operating characteristics of a fuel cell system. In principle, the reactions within the fuel processor can be either non-catalytic (thermal) or catalytic. Depending on the fuel, mode of reforming, and catalyst type, temperatures for catalytic systems typically range from 600 °C to 1000 °C [48,49]. The higher temperatures required for non-catalytic reforming can lead to formation of unwanted oxides of nitrogen. Non-catalytic reformers also require more costly materials of construction, and result in lower system efficiency due to the larger temperature difference between the fuel cell and reformer. For these reasons, they are not widely used, and are not considered further here.

Each of these modes is covered in a separate chapter (SR – Chapter 4, POX – Chapter 5, and OSR – Chapter 6). Additional modes of reforming such as CO₂ (dry) reforming (Chapter 7) and plasma reforming (Chapter 8) are also discussed in detail in this book.

1.5. THERMAL INTEGRATION OF THE FUEL PROCESSOR AND FUEL CELL

Thermal integration is an important aspect of the fuel processor. Fig. 1.3a depicts a fuel cell coupled to a catalytic POX reformer. This type of reformer operates at temperatures very close to the ~800 °C operating temperature of modern SOFCs. However, both the reformer and the fuel cell involve exothermic oxidation reactions, and heat is produced in both. This does not allow for a high degree of thermal integration and limits overall system efficiency.

Catalytic SR represents the other end of the reforming spectrum (Fig. 1.3b). Fuel is mixed with steam instead of O₂ in the reformer, to

produce a very hydrogen-rich synthesis gas. The reaction is highly endothermic, and therefore requires an external source of heat to maintain the reactor temperature. The amount of energy required is generally on the order of 22% of the lower heat of combustion of a liquid fuel [48].

OSR is actually a hybrid of POX and SR (Fig. 1.3c), and is arguably the most thermally efficient means of producing a hydrogen-rich gas stream from liquid fuels [50]. In this type of reactor, fuel, air, and steam are mixed and reacted in a thermally neutral manner such that the endothermic SR reaction is thermally balanced by the exothermic POX reactions (i.e., no net heat gain/loss).

1.6. CHALLENGES FOR FUEL CELLS AND FUEL PROCESSORS

1.6.1. Fuel Flexibility

Although fuel cells provide a clean, efficient alternative to conventional energy conversion processes, widespread use of fuel cells requires a production and distribution network for the hydrogen-rich gas stream that these systems require. As fuel cell technology becomes more economically practical, an adequate gaseous fuel supply must be provided to meet the large-scale demand. This will likely require that fuel processors be designed to generate a relatively uniform hydrogen-rich gas stream from the wide range of fuels that are available at different locations – natural gas, ethanol, gasoline, diesel, etc. These fuels contain widely varying classes of compounds – methane, aromatics, etc. – as well as varying levels of contaminants that must be removed, such as sulfur. This requires different types of catalysts and post-reformer treatment process, such as sulfur removal and water gas shift steps.

For example, consider the most widely available fuels – gasoline and diesel. Despite their logistical appeal as feedstocks for H₂ production,

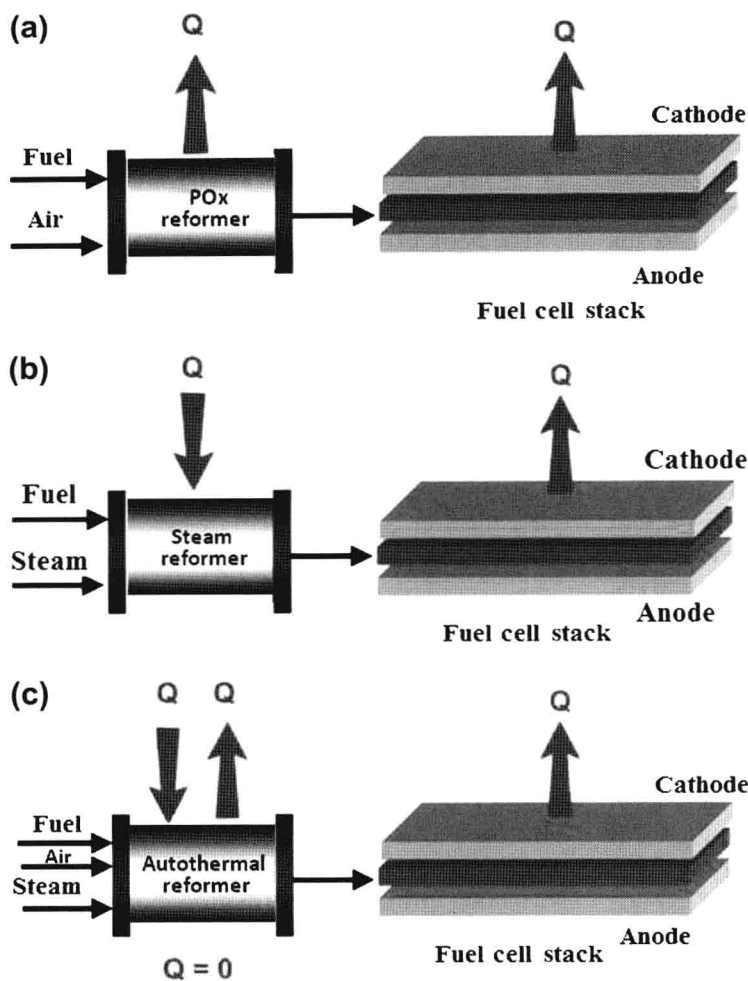


FIGURE 1.3 Thermal integration of reformer with fuel cell system: (a) partial oxidation (POX) reformer, (b) steam reformer, and (c) autothermal reformer.

these fuels are relatively difficult to reform for a variety of reasons related to both catalyst and reactor design. These fuels are complex variable mixtures of hundreds of hydrocarbon compounds containing mainly olefins, alkanes, naphthenes, and aromatics. The differing boiling points of these components can make fuel vaporization and mixing in fuel processors difficult. Pyrolytic and carbon-forming tendencies of some hydrocarbon species at the elevated temperature required to vaporize all components may lead to carbon deposition on the catalyst.

1.6.2. Catalyst

The reformer catalyst is perhaps the most critical element of the fuel processor. The catalyst must be active and selective for the fuel of choice; and stable and resistant to poisoning and sintering while subjected to transients in flow, temperature, and pressure [51,52]. For successful operation at commercial scale, the reforming process must be able to achieve high conversion of the hydrocarbon feedstock at high space velocities, as well as at high H_2 and CO selectivities.