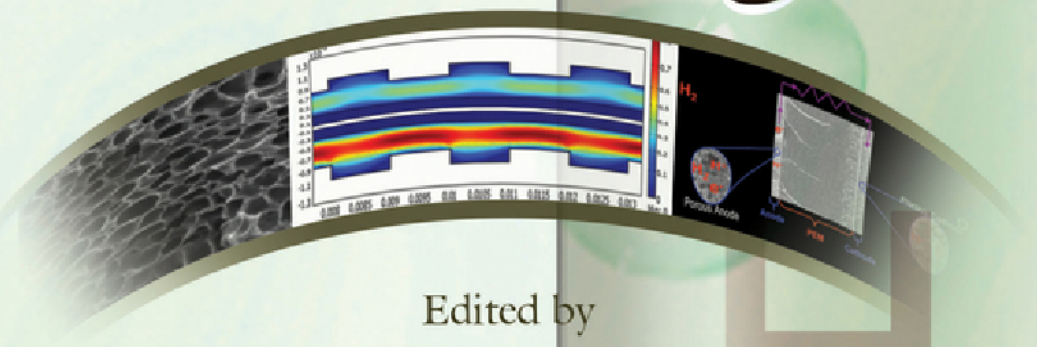


Advances in Hydrogen Production and Storage

Hydrogen Production Technologies



Edited by
Mehmet Sankir
Nurdan Demirci Sankir

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Advances in Hydrogen Production and Storage

Series Editors: Mehmet Sankir and Nurdan Demirci Sankir

Scope: Energy is one of the most important issues for humankind. Increasing energy demand, regional limitations, and serious environmental effects of the conventional energy sources provide the urgent need for new, clean, and sustainable energy. **Advances in Hydrogen Production and Storage** emphasizes the basics of renewable energy and storage as well as the cutting edge technologies employed for these applications. The series focuses mainly on hydrogen generation, photoelectrochemical solar cells, fuel cells and flow batteries.

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Hydrogen Production Technologies

Edited by
**Mehmet Sankir and
Nurdan Demirci Sankir**



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Preface

Energy is one of the most important issues for humankind. Increasing energy demand, regional limitations and serious environmental effects of conventional energy sources have brought about the need for new, clean and sustainable energy. This book series has been planned as a presentation of the basics in the areas of renewable energy and storage as well as the cutting-edge new technologies for these applications. *Hydrogen Production Technologies* is the first volume of the series due to the undeniable importance of hydrogen as a clean energy carrier. Hydrogen has been gaining more attention in both transportation and stationary power applications. Fuel cell-powered cars are on the roads and the automotive industry is demanding feasible and efficient technologies to produce hydrogen. There are various ways to produce hydrogen in a safe and cost-effective manner. This volume covers the new technologies used to obtain hydrogen more efficiently via catalytic, electrochemical, bio- and photohydrogen production and as such is a valuable component in the research area of hydrogen production. The principles and methods described herein lead to reasonable mitigation of the great majority of problems associated with hydrogen production technologies. The book is edited to be useful as a text for university students at both introductory and advanced graduate levels and as a reference text for researchers in universities and industry. The chapters are written by distinguished authors who have extensive experience in their fields. Besides researchers in the engineering area, those in the energy, materials science and chemical engineering fields have been focusing on new materials and production technologies in order to generate hydrogen in an efficient and cost-effective way. Hence a multidisciplinary approach is taken to covering the topics of this book. Readers will absolutely have a chance to compare the fundamental production techniques and learn about the pros and cons of these technologies.

The book is organized into three parts. Part I shows the catalytic and electrochemical principles involved in hydrogen production technologies. It should be clear from this part that the fundamentals and modern status

of water electrolysis, ammonia decomposition, methane reforming, steam reforming of hydrocarbons and biethanol, hydrolysis of ammonia borane and also SO_2 electrolyzer are of great importance. Therefore, their various aspects are discussed such as catalyst development, thermodynamics and kinetics of reaction mechanisms, reactor and mathematical modeling, novel membrane structures, and advanced nanoparticles. Part II is devoted to biohydrogen production. This part is designed to be a good introduction to gasification and fast pyrolysis of biomass, dark fermentation, microbial electrolysis and power production from algae. It specifically presents various catalytic formulations as well as reactor designs to overcome catalytic deactivation due to coking. In addition to gasification of wood, dried sewage sludge, and plastic waste, newly developed staged gasifiers with fewer impurities are discussed. Moreover, there is a discussion of dark fermentation using sulphate-reducing bacteria from the genus *Desulfovibrio* utilized in hydrogen production. Part II also addresses hydrogen production from electrochemically active bacteria (EAB) by decomposing organic compound into hydrogen in microbial electrolysis cells (MECs). Lastly, highly efficient harvesting of energy from algae in the forms of hydrogen and enhanced process integration reducing exergy destruction are demonstrated. The last part of the book is concerned with photohydrogen generation. Recent developments in the area of semiconductor-based nanomaterials, specifically semiconductor oxides, nitrides and metal-free semiconductor-based nanomaterials for photocatalytic hydrogen production are extensively discussed. Moreover, Part III also includes pristine and doped TiO_2 nanostructures for fast hydrogen production during photocatalytic water splitting. Finally, an earth abundant catalyst for water splitting is presented as a very promising narrow band gap visible-light photocatalyst.

Since the findings range over many useful topics specifically discussed in the book, readers from diverse fields such as chemistry, physics, materials science and engineering, mechanical and chemical engineering and also energy-focused engineering programs can benefit from this comprehensive review of the hydrogen production technologies.

Series Editors
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Part I

CATALYTIC AND ELECTROCHEMICAL HYDROGEN PRODUCTION

Hydrogen Production from Oxygenated Hydrocarbons: Review of Catalyst Development, Reaction Mechanism and Reactor Modeling

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Abstract

Hydrogen is viewed as a clean and efficient fuel for future energy generation, with an enormous amount of research being pursued to study the various routes for the production, storage, and application of hydrogen fuel. To date, diverse approaches have been employed for the production of hydrogen-rich fuel through catalytic processes using nonrenewable materials as well as sustainable feedstocks. This review of the recent literature, is intended to provide an outlook on the catalyst development, reaction mechanism and reactor modeling studies of hydrogen production using catalytic steam reforming of oxygenated hydrocarbons with focus on methanol, ethanol, and glycerol feedstocks. Various attempts to optimize the catalyst performance, including the utilization of various noble and transition active metals as well as oxide support materials, are extensively discussed. Tremendous effort has been dedicated to develop a reaction mechanism for the reforming of oxygenated hydrocarbons, with no consensus to date on the exact reaction pathway due to the complex nature of the reforming process. This review provides insights into the fundamental understanding of the reaction mechanism and the contribution of the active metals and support on the observed kinetics. Moreover, the previous literature on the modeling and simulation of the hydrogen production process is also reviewed.

Keywords: Hydrogen production, oxygenated hydrocarbons, catalyst development, reaction kinetics, reaction mechanism, reactor modeling

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1.1 Introduction

The global reliance on fossil fuels as the main energy source for power generation, transportation, and as a feedstock for chemical industries is widely increasing with the discoveries of new fossil fuel reserves and the technological advancement in their production and application. According to the recent annual energy outlook released in 2014 by the International Energy Agency (IEA), fossil fuels are projected to supply more than 80% of the world total energy by 2040. However, fossil fuel-based energy generation has increased the concentration of greenhouse gas emissions to an alarming level of 400 ppm in 2013 [1]. The continued increasing levels of anthropogenic greenhouse gases in the atmosphere will ultimately cause further weather changes, resulting in severe impacts on life on earth; therefore, combating climate change requires sustainable development of green technologies and policies to mitigate climate change. In accordance with the Paris Climate Conference (COP21) of 2015, several countries have pledged to reduce their emission levels to possibly achieve a 2 °C scenario (2DS) and cut the emissions to 60% by 2100, corresponding to cumulative CO₂ emissions of 1000 GtCO₂. In order to achieve such objectives a portfolio of low-carbon technologies has to be deployed to reach the 2DS, consisting of energy efficiency, fuel switching, and renewable energies. According to the 2016 energy technology perspective report issued by the IEA, the contribution toward the reduction of the cumulative CO₂ emissions in the 2DS over the period 2013 to 2050 is estimated to be 38% from electricity efficiency, 12% for carbon capture and sequestration (CCS), and around 32% should come from the deployment of renewable energy sources. To establish clean energy for the future, the development of low carbon energy supply is urgently required. Among the possible alternatives, hydrogen has the potential to provide an ideal energy carrier that can meet the increasing global demand for energy and efficiently replace the existing fossil fuels [2, 3]. Hydrogen can provide an energy of 122 kJ/g, which is almost three times higher than hydrocarbon fuels [4], and is projected to contribute 34% of the total renewable resources in 2050 [5]. The application of hydrogen in the transportation and power generation sectors is receiving growing interest from both the technological and the policy-making aspects [6–8]. The contribution of hydrogen as a fuel for the transportation sector is mainly driven by the great achievements in fuel cell technology and the development of internal combustion engines that uses hydrogen fuel [9–12]. Fuel cell-based engines have three times higher efficiency than conventional gasoline engines due to the excellent characteristics of hydrogen as an energy

carrier [13], in addition to the outstanding performance of hydrogen as a transportation fuel [14]. Hydrogen fuel being a gas at normal temperature and pressure, as compared to liquid hydrocarbon fuels, presents a major challenge for safe storage and transportation [15, 16]. Traditional storage schemes require energy-intensive techniques and have great safety concerns; however, the latest developments in the methods and technologies of the materials used for hydrogen storage are promising for realizing the hydrogen economy. Several review papers have described the current status and future trends in hydrogen storage materials [15, 17, 18]. Hydrogen can be produced from various energy sources using different processes, which could be categorized into renewable and nonrenewable resources. Hydrogen production from fossil fuel derivatives, such as methane and coal through gasification and thermocatalytic processes, is considered the major source for nonrenewable hydrogen production, representing more than 95% of the hydrogen produced to date [19]. In addition to being nonrenewable, hydrogen produced from fossil fuel resources contributes to global warming by releasing CO_2 during the production process. On the other hand, biomass is considered as a sustainable route for hydrogen production with less net CO_2 produced due to the fact that the CO_2 released from the conversion of biomass has already been naturally captured from the atmosphere. In addition to the most widely used thermochemical technology, other methods, such as the electrolysis of water, have also been used for hydrogen production, with a major drawback of being highly energy intensive and having a low efficiency of around 25% [20, 21]. Other technologies, such as the photobiological techniques, are also reported based on the photosynthetic stimulation of some types of bacteria to release hydrogen; however, the sluggish release rate of hydrogen is considered a major challenge for these technologies [22–24]. Several review papers are available that give a detailed overview of the different hydrogen generation technologies [14, 25, 26]. Dincer *et al.* [27] followed a comparative assessment approach to evaluate several hydrogen production schemes such as natural gas reforming, electrolysis, coal and biomass gasification. The assessment criteria included environmental, economic and social impacts of these various methods. It was concluded that for the case of Turkey, biomass gasification has the best energy efficiency, whereas electrolysis methods were found to be less attractive when the hydrogen cost is considered.

This chapter aims at reviewing the sustainable and environmentally friendly hydrogen production from the steam reforming of oxygenated hydrocarbons, with a special focus on methanol, ethanol and glycerol, to recapitulate the state of the art in this field, and summarize the research

conducted in the past five years (2012 to 2016) in order to get deep insights into the promising future for these technologies. The literature pertaining to the catalyst development for the steam reforming process, reaction mechanism, reactor modeling and simulations is thoroughly reviewed following a comparative analysis approach whenever possible.

1.2 Catalyst Development for the Steam Reforming Process

The catalyst development is considered the heart of sustainable hydrogen production through the steam reforming of oxygenated hydrocarbons. The hydrogen production rate, purity, and the selectivity of the reforming process are significantly impacted by the characteristics of the catalyst used. This crucial role of the catalyst has been highlighted by the numerous research projects conducted over the past years to understand the fundamentals of the catalytic process, and to develop highly efficient catalysts that can increase the overall conversion, improve hydrogen yield and prolong their lifetime [28, 29]. There are certain catalytic traits that need to exist for an efficient catalyst to be used in the steam reforming hydrogen production. These characteristics are prominently dependent on the nature of the oxygenated hydrocarbon feed (i.e., methanol, ethanol or glycerol) as well as the feed purity (i.e., crude versus pure) [30]. However, there are general requirements for catalytic surfaces such as: (1) the activity for C-C bond cleavage to produce CO, CO₂, and CH₄, (2) steam reforming of intermediates to produce hydrogen, and (3) the ability to produce free oxygen while preventing coke formation as well as C-O bond creation [31, 32]. Based on the contribution in the catalytic reforming reaction, there are three distinct parts of the catalyst: the active metal, the support, and the metal-support interactions. Control of the interaction between the metal and support is essential to improve the dispersion of the active sites and consequently achieve a better reaction rate and hydrogen yield. It was found that it is not only the nature of the individual support and metal sites that affects the reforming reaction but rather the interface that plays a vital role as reported recently [33]. In the following section we will thoroughly review and summarize the work that been performed over the past five years in the development of active metals and support materials for the catalytic transformation of oxygenated hydrocarbons to hydrogen. As stated earlier, this review chapter will focus on methanol, ethanol and glycerol as models for the oxygenated hydrocarbon feed; thus, accordingly, this section will be discussed in light of these three contexts.

1.2.1 Catalyst Development for the Steam Reforming of Methanol (SRM)

A very good review paper by Sá *et al.* [29] has been published which summarizes the development on catalysts used for the SRM process reported before 2010. In this section we will mainly present the latest work conducted after 2010 to provide the most recent perspective in order to keep up to date with the rapid progress in the research related to the catalyst development for the SRM process. The most common catalyst for SRM is Cu-based catalyst. Tremendous effort has been dedicated to understanding the catalytic reforming over Cu-based catalysts and to prepare efficient catalysts with high dispersion, high surface area, and small particle sizes. Several approaches are available to accomplish these objectives such as investigating novel synthesis methods [34], using promoters [33, 35], utilizing active support materials and the optimization of the operating conditions for higher hydrogen yield and improved catalyst stability [36, 37]. Table 1.1 summarizes the recent literature pertaining to the heterogeneous catalyst development for SRM process using Cu-based catalysts. Researchers in this field have been focusing on improving certain characteristics of the Cu-based catalysts such as the particle size, support surface area, and Cu dispersion. To achieve these objectives several approaches were used, including the optimization of the synthesis method, using support promoting materials, and the utilization of novel non-oxide supports. Cu supported on ZnO has gained considerable attention in the literature owing to its high activity in SRM [38]. The ZnO support provides the required surface area to disperse the Cu metals and prevent its agglomeration, and most importantly increase the reducibility of Cu by acting as a withdrawing agent for H atoms [37, 39]. A recent study suggested that increasing the surface area of the ZnO support by varying its calcination temperature can significantly improve the Cu dispersion, whereas the reducibility of the ZnO support could be controlled by changing the Zn precursor gel [39]. The selectivity of the Cu/ZnO catalyst prepared using highly polar precursor solution of Zn acetate as opposed to Zn nitrate was proven to be even higher than the commercial Cu/ZnO/Al₂O₃ catalyst [39], which was attributed to the increase in the catalyst reducibility. The effects of the support pretreatments, such as calcination conditions [40] and anodic oxidation [41], have also been studied in the literature. Nakajima *et al.* [42] have also proposed a new approach for the fabrication of Cu/ZnO catalyst by preparing ZnO nanowires on quartz substrates and then using UV laser to grow Cu on the surface of ZnO nanowires. The careful control of the ZnO nanowires length has shown an improved selectivity toward hydrogen

Table 1.1 Summary of SRM reaction over various metal-oxide supported catalyst.

Catalyst	Preparation method	Steam/methanol	Temperature (°C)	Methanol conversion (%)	Remarks	Ref.
CuO/ZnO/ZrO ₂ /Al ₂ O ₃	Sonochemically co-precipitation	1.5	200	100	Ultrasonic power-enhanced surface area, metal dispersion and reduced particle sizes	[34]
CuO-ZnO-Al ₂ O ₃	Microwave-assisted solution combustion	1.5	240	100	Microwave irradiation and fuel/nitrate ratio resulted in higher crystallinity, surface area, smaller particle size and hence significantly improved the catalyst stability	[110]
Cu0.07Fe0.93Al ₂ O ₄	Solution combustion synthesis	1.1	330	70	Solution combustion synthesis is better than the impregnation method for Cu-Metal-Al ₂ O ₃ , however, the impregnation method produced catalyst with relatively higher surface area than the combustion-based method. The catalyst deactivation was evident due to sintering, but the turnover frequency of the combustion synthesis route was higher than the impregnation method.	[111]
Cu0.10Fe0.90Al ₂ O ₄				98		
Cu0.15Fe0.85Al ₂ O ₄				92		
Cu0.1Mg0.9Al ₂ O ₄				72		
Cu0.1Mn0.9Al ₂ O ₄				32		
Cu0.1Zn0.9Al ₂ O ₄				70		
Cu0.1/Fe0.9/Al ₂ O ₄				88		
	Incipient wetness impregnation					

Ni_xMg_y	Modified incipient wetness	3	600	97.4	[79]
Cu ₃₀ Zn ₆₀ Al ₁₀	Co-precipitation method	1.2	250	57	[112]
Cu ₄₀ Zn ₅₀ Al ₁₀				60	
Cu ₅₀ Zn ₄₀ Al ₁₀				66	
Cu ₆₀ Zn ₃₀ Al ₁₀				62	
Cu ₅₀ Zn ₃₀ Zr ₁₀ Al ₁₀				75	
Cu ₅₀ Zn ₃₀ Ce ₁₀ Al ₁₀				60	
CuO/CeO ₂ (5.5% Cu)	Incipient wetness method	-	300	73	[63]

(Continued)

Table 1.1 Cont.

Catalyst	Preparation method	Steam/methanol	Temperature (°C)	Methanol conversion (%)	Remarks	Ref.
3% Ni/Cu/ZrO ₂	Successive impregnation method	-	400	83	The successive impregnation of bimetallic Ni/Cu on ZrO ₂ support is performed. Ni loading of 15 wt% was found to be the optimum for both the activity and selectivity due to the formation of Cu in the core and Ni on the shell side of the catalyst.	[100]
15% Ni/Cu/ZrO ₂				90		
30% Ni/Cu/ZrO ₂				98		
Ce0.5Zr0.33Gd0.166O ₂	Surfactant-assisted method	2	550	40	A standard wet impregnation technique was used to prepare the catalyst. Slow heating was employed to dry the impregnated samples.	[77]
Ce0.5Zr0.33Gd0.166O ₂				67		
Ni _{1-x} Cu _x /Fe ₂ O ₄ (x = 0, 0.5, and 1.0)	Solid-state reaction technique	1.5	360	-	The effect of varying the reduction temperature between 240 to 500 °C on the properties of the catalyst was investigated	[104]
CuO/ZnO (Zinc Acetate precursor calcined at 300 °C)	Modified hydrothermal method	2.5	220	11.7	The polarity of the catalyst was controlled by changing the Zn precursor, while the surface area was tuned by changing the calcination temperature. The increased polarity of the ZnO improved the reduction ability of the CuO catalyst and hence increased the selectivity. Also, the increase in ZnO surface area (higher calcination temperature) has promoted the Cu dispersion and Cu specific surface area.	[39]
CuO/ZnO (Zinc Acetate precursor calcined at 350 °C)				13.8		
CuO/ZnO (Zinc Acetate precursor calcined at 375 °C)				15.9		
CuO/ZnO (Zinc Nitrate precursor calcined at 375 °C)				14.7		