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Spinel Mixed Oxides for Chemical-Loop Reforming: From Solid State to Potential Application

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SECTION 3

ADVANCED SUSTAINABLE
CHEMICAL PROCESSES
AND CATALYSTS
FOR ENVIRONMENT
PROTECTION

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Spinel Mixed Oxides for Chemical-Loop Reforming: From Solid State to Potential Application

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1 INTRODUCTION

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Current processes for the industrial production of hydrogen are mainly based on the reforming of natural gas/naphtha or coal gasification. Such processes are highly energy demanding. Hence, less energy-intensive and more sustainable technologies, exploiting renewable feedstocks (such as biomass, bio-alcohols, and water) and renewable primary energy sources (e.g., sunlight, wind, wave, or hydropower), appear to be very attractive for both industrial and consumer applications. A variety of new technologies offering a nonfossil based route for hydrogen production are in a different stage of development, and each offers unique opportunities, benefits, and challenges [1–10].

p0015

Chemical-looping approach for hydrogen production is one of the possible ways to produce high-purity H₂ starting from either conventional or renewable sources. The main principle of any looping technology is ingrained in the second law of thermodynamics and applied to enhance exergy efficiency of the process [11]. Initially, the chemical-looping process for hydrogen generation was introduced as a “steam-iron” process in 1913 by Lane et al. [11,12]. At present, any process that aims to produce hydrogen via looping technology is referred to a “chemical-looping hydrogen” (CLH), or “chemical-looping water splitting” (CLWS) process, which usually consists of two spatially or temporarily separated steps: reduction and oxidation. Thus, different from a classical steam methane reforming (SMR), separation costs can be avoided by splitting the process into two alternated steps in order to separate H₂ and CO_x streams. Generally, the reduction step is used to transfer oxygen from an oxygen carrier material to a reducing fuel. The reduced oxygen carrier is then regenerated with steam, which enables the production of high-purity hydrogen without an additional separation step. The chemical-looping process can be performed using a number of different reductants, such as

gas from coal [13] or biomass [14–16] gasification, light hydrocarbons reforming [17], methane [18–20], a CH₄/CO₂ and CH₄/H₂ mixture [20,21], pyrolysis oil [22,23], methanol [24], and pure H₂ (as a method for H₂ storage) [25,26]. Furthermore, the nature of the oxide, used as the ionic oxygen and electron carrier, and the reaction conditions are important parameters because they determine the potential for low costs and high efficiency of this process in order to have a commercial impact.

2 HYDROGEN APPLICATIONS

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Hydrogen is one of the key starting materials used in the chemical industry with an annual worldwide production of about 50 million tons. Currently, the largest amount (~95%) of the total manufactured hydrogen is consumed mainly by two industrial segments: the chemical sector, accounting for 65% of the market share (ammonia and methanol synthesis ~63%; liquid hydrocarbons and higher alcohols synthesis ~2%), and the refining sector, which accounts for 30% of the market share (hydrotreating and hydrocracking processes for obtaining high-grade petrochemical products). The other present uses, with ~5% of the total consumption, include the food industry (sorbitol and fat processing), the metallurgical industry (direct reduction of iron ore), the semiconductor industry, etc. (Fig. 14.1).

p0025

In the near future, the possibility to produce hydrogen in a sustainable manner on the larger scale will boost research landmarks to search for new technological platforms for direct transformation of captured CO₂ to its hydrogenated C1-counterparts: formic acid (HCOOH), formaldehyde (H₂CO), methanol (CH₃OH), and methane (CH₄) [27]. Highly reduced methanol is indeed the key molecule for the methanol economy and remains obviously a target molecule of choice in terms of its further use in MTH-processes, as well as H₂-storage and carriers in

3. ADVANCED SUSTAINABLE CHEMICAL PROCESSES AND CATALYSTS FOR ENVIRONMENT PROTECTION





INDUSTRIAL SECTOR	KEY APPLICATIONS	H ₂ demand
 CHEMICAL ~ 65%	-AMMONIA PRODUCTION (mix. H ₂ + N ₂) -METHANOL PRODUCTION (mix. H ₂ + CO)	
 REFINING ~ 30%	-HYDROTREATING (S,N,O-removal; olefins and aromatics saturation) - HYDROCRACKING (break C-C bond)	
 OTHERS ~ 5%	-FOOD INDUSTRY (hardening of edible oil) -METALLURGICAL INDUSTRY (iron reduction; blanketing gas; forming gas) -SEMICONDUCTOR INDUSTRY, etc.	

FIG. 14.1 Main segments of hydrogen consumption.

fuel cells. It is already produced, albeit mainly from natural gas and coal, at a yearly >50Mt-scale, with a forecasted annual growth of 4% [28]. Methane, the totally reduced product from CO₂, is still considered as a potent molecule in a power-to-gas concept [29], in which superfluously produced energy by nuclear sources or irregularly produced wind, water, and solar (WWS) electricity may be converted and stored in the chemical bonds of the methane molecule. The advantage of this concept is that methane can be fed in the already available natural gas infrastructure [27,30].

In conclusion, there is a fast-growing need for increased hydrogen production, because H₂ itself may become an important “energy vector” with key applications as a carbon-free fuel and as a fuel for hydrogen-driven fuel cells for automotive uses. However, there are still several major problems to be overcome before it can be used in this way, including its manufacture, storage, and distribution.

2.1 Fuel Cells

Fuel cells are devices that generate electricity based on a chemical reaction and are often referred to as continuously operating batteries. They exploit electrolysis reactions in a similar manner to traditional batteries, however, the reagents are constantly supplied to the cell. This is determining the difference compared to the traditional dischargeable batteries. There are several kinds of fuel cells, though the main operating principle remains the same: hydrogen atoms (or other fuels) at the anode break down to form electrons and H⁺ ions; the latter ones migrate through the electrolyte/membrane to the cathode, where two H⁺ ions combine with oxygen to form water (also emitting heat), while the electrons run through the electrical circuit, producing a current (Fig. 14.2).

Nevertheless, its applications can vary depending on the type of hydrogen fed to the

3. ADVANCED SUSTAINABLE CHEMICAL PROCESSES AND CATALYSTS FOR ENVIRONMENT PROTECTION

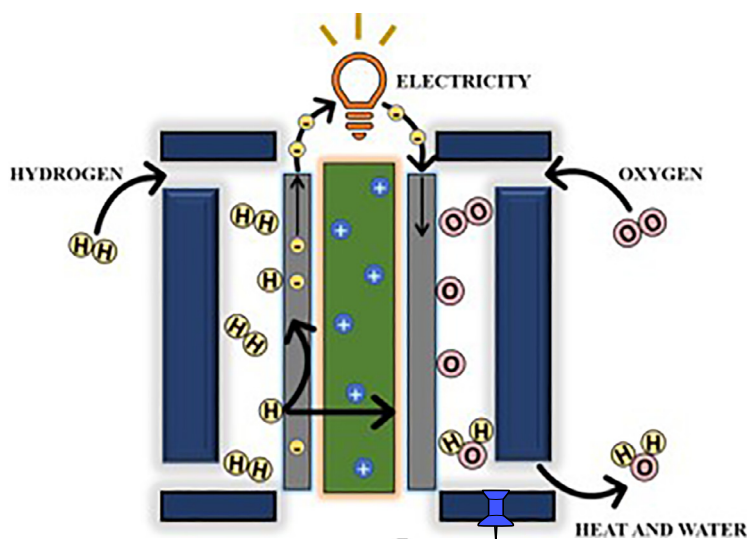


FIG. 14.2 General scheme of the fuel cell technology.

anode (they can be chemical elements containing hydrogen) and the nature of the electrolytes (Fig. 14.3).

3 HYDROGEN PRODUCTION

3.1 Common Feedstocks

Hydrogen can be produced from different resources, including conventional and well-known fossil fuels, such as natural gas, naphtha and coal, or from renewable feedstocks or energy sources like biomass, wind, solar, and geothermal energy, etc. Currently, many new technologies, which offer sustainable and nonfossil-based itineraries for hydrogen production, are at a different stage of development, and each one brings its own benefits, opportunities, and challenges. A list of the various feedstocks and process technologies is presented in Fig. 14.4.

3.2 Common Processes for H₂ Production

Hydrogen can be produced using many different processes (as illustrated in Fig. 14.5). Thermochemical processes use heat and chemical

reactions to release hydrogen from organic materials such as fossil fuels and biomass. Water (H₂O) can be split into hydrogen (H₂) and oxygen (O₂) using electrolysis or solar energy. Microorganisms such as bacteria and algae can produce hydrogen through biological processes. This section encompasses the most relevant information about the existing processes to manufacture hydrogen.

3.3 Hydrogen Via Reforming Processes

Reforming processes are based on the endothermic or exothermic conversion of the feedstock materials with H₂O/CO₂/O₂ converting into a synthetic gas mixture (CO+H₂). The most commonly used feedstocks for the reforming processes are methane or other light hydrocarbons obtained from oil. Several chemical processes have been developed to produce hydrogen via the reforming route:

- | | |
|------------------------------------|-------|
| (1) Steam reforming (SMR) | o0010 |
| (2) Auto thermal reforming (ATR) | o0015 |
| (3) Partial oxidation (POX) | o0020 |
| (4) Dry reforming of methane (DMR) | o0025 |

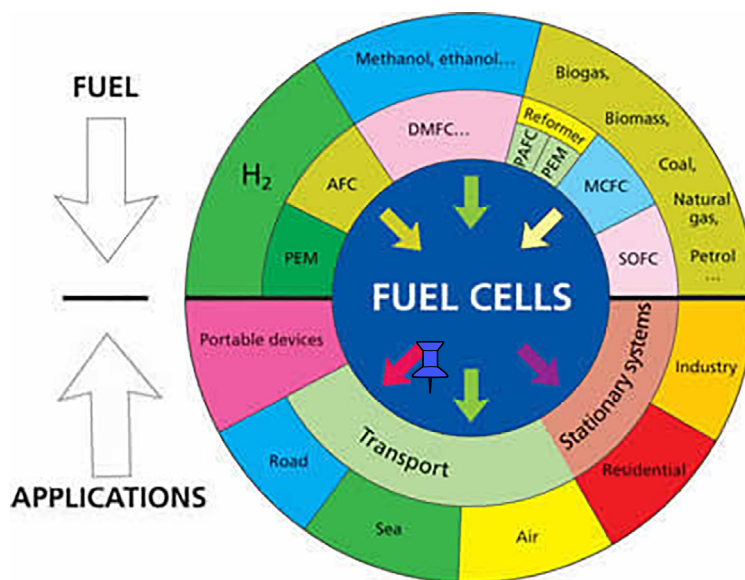


FIG. 14.3 Lower segment: main application of the fuel cell technology; Upper segment: fuel and fuel cell types. AFC, alkaline (especially in the space sector); DMFC, direct membrane; MCFC, molten carbonate; PAFC, phosphoric acid; PEMFC, polymer exchange membrane; SOFC, solid oxide. From <https://ec.europa.eu>.

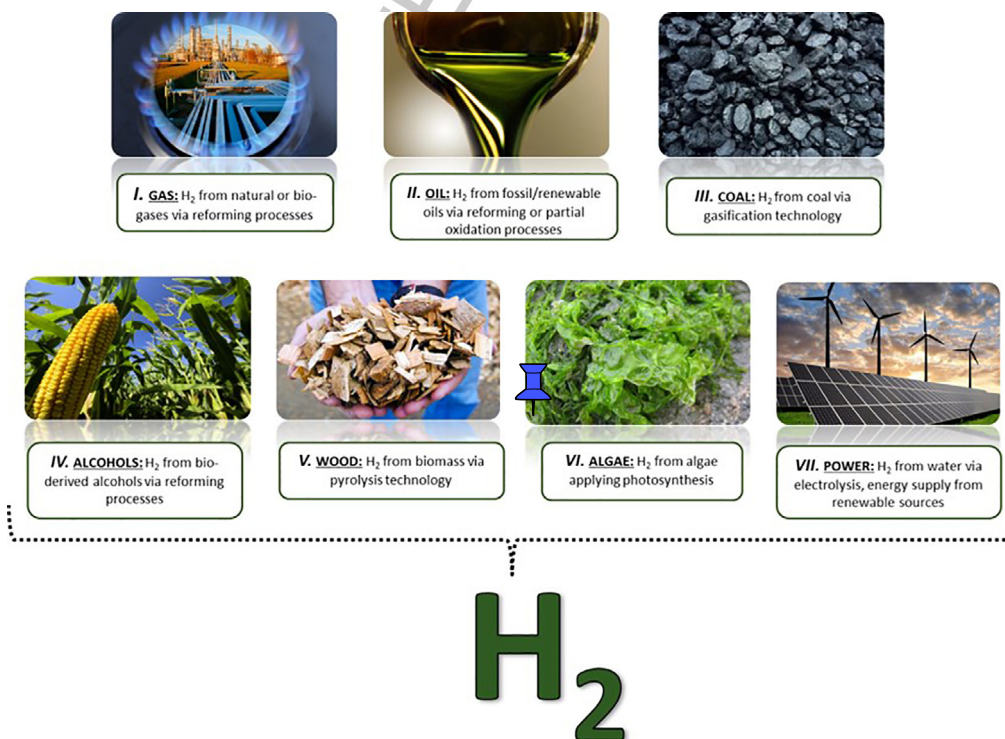


FIG. 14.4 Summary of the various feedstocks and process alternatives for H_2 production. Inspired by T. Riis, E.F. Hagen, J.S. Vie, P.J.S. Vie, Ø. Ulleberg, G. Sandrock, *Hydrogen Production and Storage; R&D Priorities and Gaps*, OECD/IEA, 2006.

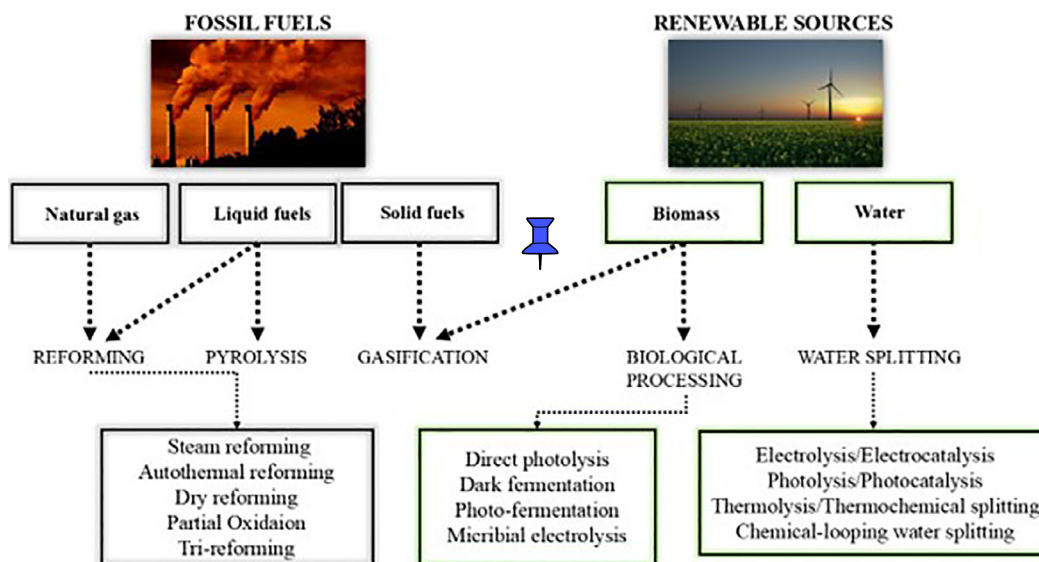


FIG. 14.5 An overview of existing hydrogen production processes from different sources. *Inspired by D. Yamaguchi, L. Tang, N. Burke, K. Chiang, L. Rye, T. Hadley, S. Lim, Small Scale Hydrogen Production From Metal-Metal Oxide Redox Cycles, INTECH, 2012.*

- o0030 (5) Combined reforming of methane (CMR)
- o0035 (6) Reforming with membrane
- o0040 (7) Tri-reforming of methane (TMR) [31]

p0095 The first three are widely used industrial processes, whereas the last four are more recent innovative processes developed with the aim to minimize environmental impact and energy consumption together with the improvements of already existing methods.

s0045 3.3.1 Steam Methane Reforming (SMR) and Water Gas Shift (WGS) Reaction



p0105 Steam methane reforming (SMR) is the most common way to produce a hydrogen-rich syngas mixture ($\text{H}_2 + \text{CO}$). A conventional steam reformer unit consists of several hundred fixed-bed reactor tubes filled with a catalyst, which can vary in size and geometry. High temperatures ($>600^\circ\text{C}$) and low pressures favor the formation of H_2 and CO products (Le Chatelier's

principle). However, in practice, the natural gas steam reformer is operated under the pressure of about 20–30 atm (for kinetic reasons), with an exit temperature of 800–870°C (but the tube wall temperature can range from 700°C up to a maximum hot spot of 920°C), where methane and steam are converted into synthesis gas (mixture of CO and H_2). Steam methane reforming is a catalytic process and catalyst properties are dictated by the severe operating conditions, that is, temperatures of 450–950°C and steam partial pressures up to 30 bar. Conventional steam reforming catalysts are Ni-based catalysts with 10–20 wt.% Ni supported on $\alpha\text{-Al}_2\text{O}_3$, calcium or magnesium aluminate with a typical lifetime of 3–5 years. Cobalt and noble metals (Ru, Rh, Pt, and Pd) are also known to be active, however they have not found many applications as SMR catalysts due to their elevated costs. On the other hand, attempts to use cheaper and abundant nonmetallic catalysts have not had commercial success because of the low activity.

p0110 Normally, the subsequent stage of the SMR process includes WGS reactions which further convert carbon monoxide to carbon dioxide, while generating more hydrogen.



p0115 In the first stage, where a high temperature shift reaction is taking place, the gas is mixed with steam and passed over an Fe/Cr or Fe/Cr/Mg mixed oxide catalyst at $T = 300\text{--}450^\circ\text{C}$ in a fixed bed reactor, which decreases the carbon monoxide concentration down to 2%–3%. In the second stage, the low temperature shift reaction, the mixture of gases is passed over a Cu/Zn oxide catalyst at $T = 190\text{--}220^\circ\text{C}$, where the carbon monoxide concentration is reduced to 0.1%–0.2%. Further hydrogen purification can be achieved using:

- u0010 – Methanation
- u0015 – Pressure swing adsorption (PSA)
- u0020 – Membrane reactors

s0050 3.3.2 Steam Naphtha Reforming

p0135 If naphtha is used as the feedstock, an extra reforming stage is needed. The naphtha is first heated to form a vapor, which is then mixed with steam and passed through tubes, heated at $T = 450\text{--}500^\circ\text{C}$ and packed with a catalyst, nickel supported on a mixture of aluminum and magnesium oxides. The main product is methane together with carbon oxides (CO_x), which is then processed by SMR, as if it were natural gas, followed by the shift reaction.

s0055 3.3.3 Dry Methane Reforming (DMR)



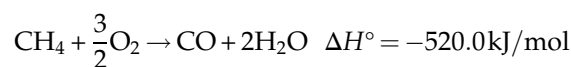
p0145 The DMR process is characterized by a very low intrinsic activity, in addition to the simultaneous occurrence of the reverse water gas shift (RWGS) reaction resulting in a syngas ratio less than a unity. Dry reforming of methane has been investigated with noble (Rh, Ru, Pd, and Pt) and non-noble metal- (Ni, Co, and Fe) -based catalysts. Noble metal catalysts (Pt/support) [32] have

drawn attention for their superior coking resistance, higher stability, and activity, especially for higher temperature applications. However, for large scale industrial applications, development of the active catalyst is still under investigation.

3.3.4 Autothermal Reforming (ATR)

s0060

Autothermal reforming (ATR) is an important industrial process used to produce syngas with a low H_2/CO ratio (from 1.5 to 3) desired for synthesis of methanol and higher molecular-weight hydrocarbons (via The Fischer-Tropsch process). The main concept is the combination of noncatalytic partial oxidation and adiabatic catalytic steam reforming, where the reactor temperature is maintained using the heat emitted from the partial oxidation of the hydrocarbon feedstock, typically methane, with a sub-stoichiometric amount of oxygen.

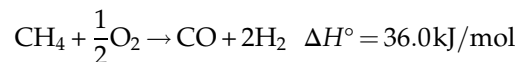


This process was developed by Haldor Topsøe A/S, with the aim to perform the POX (partial oxidation) and the SR (steam reforming) in a single ATR reactor. The very high temperatures in the ATR unit require a high thermal stability of the catalyst, which is typically a nickel-based catalyst on a stabilized Al or Mg-Al support.

p0155

3.3.5 Partial Oxidation (POX)

s0065



An alternative way to produce hydrogen is based on the partial oxidation of a sub-stoichiometric fuel-air mixture which results in a formation of H_2 -rich syngas. Partial oxidation is an exothermic reaction and, thus, is considered to be more economically feasible than the processes of steam or dry reforming. The exothermic nature of the reaction has certain

p0165

drawbacks because it induces hot spots on catalysts, arising from a poor heat removal rate, which causes difficulties in operation control. A difference is made between *thermal partial oxidation* (TPOX) and *catalytic partial oxidation* (CPOX).

s0070 **3.3.6 Thermal (Noncatalytic) Partial Oxidation**

p0170 TPOX is a noncatalytic process in which the feed is partially combusted with a sub-stoichiometric amount of air, oxygen, or enriched air to obtain a CO+H₂ mixture, where the production of syngas depends on the oxygen-to-fuel ratio at an operating temperature range of 1200–1500°C. Feedstocks used for the TPOX can be almost any carbonaceous material, from natural gas through liquid feeds such as fuel oils, gas oils, and coal. A noncatalytic partial oxidation process was developed by Texaco and Shell which results in high syngas yields at high temperature and pressures [33].

s0075 **3.3.7 Catalytic Partial Oxidation**

p0175 CPOX is a catalytic process in which the feed with sub-stoichiometric amount of oxygen (or air) is catalytically converted into a CO+H₂ mixture. The use of a catalyst lowers the required reaction temperature down to 800–900°C. Commonly used catalysts are noble (Pt, Rh, Ir, Pd) or nonnoble (Ni, Co) metal-based catalysts. Catalytic partial oxidation can be performed only if the sulfur content of the feed is below 50 ppm, because higher sulfur contents would poison the catalyst (in such cases, noncatalytic partial oxidation is more suitable for the use).

s0080 **4 HYDROGEN VIA ALTERNATIVE PROCESSES**

s0085 **4.1 Water Splitting**

p0180 Water splitting is a process that enables the production of hydrogen by direct water decomposition in its elements. The energy required to cleave H—O—H bonds can be supplied by

different power sources: electrical (current), thermal (heat), or light (electromagnetic radiation). Generally, the difference in water splitting processes is made whenever one or another type of energy source is applied to conduct the reaction, referred to as electrolysis, thermolysis, or photolysis. Electrolytic water splitting is driven by passing the electrical current through the water, where conversion of the electrical energy to chemical energy takes place at the electrode-solution interface through charge transfer reactions in a unit called an electrolyser [34]. Water reacts at the anode to form oxygen and protons, whereas a hydrogen evolution reaction takes place at the cathode. Only 3.9% of the world's hydrogen demand is satisfied by electrolysis. Although, compared with the conventional SMR, the electrolytic water splitting is described as a less environmentally harmful process with a “zero” CO₂ emission (because O₂ is the only by-product), electrolyzers generally powered by the electricity, which is predominately produced by the combustion of coal or natural gas, resulting in the release of CO₂ as a byproduct. Therefore, today's research is increasingly oriented on utilizing renewable harvesting technologies (wind turbines or photovoltaics) to drive the electrochemical/catalytic water-splitting reaction. Photochemical [35,36]/photocatalytic [37,38] water splitting is a promising option for hydrogen production, which is oriented on the reduction of CO₂-emission and applications of renewable resources such as water and sunlight. The most important criteria for solar-driven water splitting reactions is the electronic bandgap alignment of the photosensitive material with the redox potential of water [37]. In general, the presence of transition metal cations with a d⁰ electronic configuration (Ta⁵⁺, Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, Ta⁵⁺, W⁶⁺, and Mo⁶⁺), or metal cations with a d¹⁰ electronic configuration (In³⁺, Sn⁴⁺, Ga³⁺, and Ge⁴⁺) is considered to be important for the efficient photocatalytic materials, the empty d or sp orbitals of which form the bottom of the respective conduction bands [36]. Over the last decades, significant progress in this field

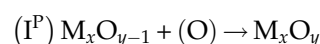
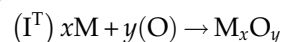
has been made by an increasing number of research groups where the topic was thoroughly reviewed [39–41].

p0185 Thermal or thermochemical water splitting is another alternative technology to produce hydrogen from water with potentially low or no greenhouse gas emissions [42,43]. This technology has been extensively studied by many research groups, and more than 300 water-splitting cycles with different operating parameters, engineering challenges, and hydrogen production opportunities are described in the literature. Thermochemical water splitting processes require high temperatures (500–2000°C) to drive a series of chemical reactions, which lead to hydrogen evolution. The chemicals used in the process are reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen. This technology is an appealing pathway to produce hydrogen-utilizing waste heat from existing nuclear power stations or concentrated (using a field of mirror “heliostats”) solar power. However, a realization of renewable-energy solutions for the water splitting reactions on a larger scale remains a challenge, which is dictated by the overall economy of the process and heavily depends on further developments of cost-effectiveness and environmentally benign technologies. Thermochemical water splitting has stimulated the development and growth of a series of new looping technologies that will be described in the next section.

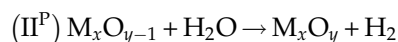
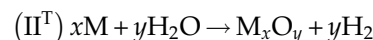
s0090 4.2 Hydrogen Via Chemical-Looping (CL) Processes

p0190 Chemical-looping processes are alternative processes aimed at generating heat and power (chemical-looping combustion, CLC) or to produce a CO+H₂ mixture (chemical-looping reforming, CLR) or high-purity H₂ (chemical-looping hydrogen/chemical-looping water splitting, CLH/CLWS) via looping technology that usually consists of two temporarily or spatially separated steps: reduction and oxidation. During the reduction step, a transfer of oxygen to fuel is

mediated by a metal oxide as an oxygen carrier (OC) material (Me_xO_y), which is put in contact with a reducing stream. The OC is thus reduced and at the same time converts fuel into products, mainly CO_x, H₂O, and H₂ (products distribution strongly depends on nature of the reducing agent as well as the nature of the oxygen carrier). Subsequent oxidation steps are performed over the previously reduced material utilizing air/pure oxygen (I):



or water steam, referred to water splitting technology (II):



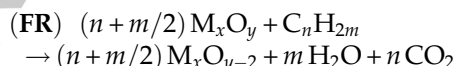
(I^T, II^T), where (^T) index refers to a total reduction of OC, u0025

(I^P, II^P), where (^P) index refers to a partial reduction of OC. u0030

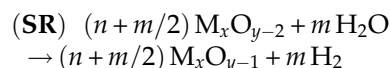
An oxidation step is needed to restore the oxygen carrier material to its original oxidation state (Me_xO_y) and to produce H₂ (when the oxidation step is carried out with steam). A difference is made whenever steam from air or water is used to regenerate the oxygen carrier material. The oxidation step performed with air is varied between steam reforming coupled with the chemical-looping combustion process (SR-CLC), where CLC is used to supply energy, which is needed for the conventional catalytic steam reforming, and the chemical-looping reforming process (CLR), where main products from the chemical-looping system are an H₂ and CO mixture. Other processes use some oxygen-depleted materials to react with water steam to generate pure H₂, also known as “water splitting.” In this category, it can be found in chemical-looping hydrogen (CLH), or one step decarbonization (OSD) processes, and the so-called chemical-looping gasification p0205

technologies: syngas chemical-looping process (SCL) and coal direct chemical-looping process (CDCL), etc. Usually the later processes need several oxidation steps, like an air treatment, which sometimes is required for the final regeneration of the oxygen carrier material [44]. Several in-depth reviews [45–47] summarize information on the existing chemical-looping processes aligned to produce high purity hydrogen, and offer both the use of renewable and CO₂-neutral feedstocks, as well as efficient CO₂ sequestration capabilities [46].

as gas resulting from coal [13] or biomass [14–16] gasification, light hydrocarbons reforming [17], methane [18–20], CH₄/CO₂ and CH₄/H₂ mixture [20,21], pyrolysis oil [22,23], light alcohols [48–56], and pure H₂ (as a method for H₂ storage) [25,26]. Different from a classical reforming, separation costs can be avoided by splitting the process into two/three alternated steps in order to separate H₂/CO_x streams and fully re-oxidize the oxygen carrier materials (Fig. 14.6). Generally, the reducing fuel (C_nH_{2m}) is fed to the feed reactor (FR), where it reacts with the oxygen carrier material (M_xO_y) according to the following equation:



After the first step, previously reduced oxygen carrier material is transferred to the steam reactor (SR), where it is oxidized by a water steam to restore its original oxidation state:



5 CHEMICAL-LOOP REFORMING (CLR) FOR HYDROGEN GENERATION

CLR for hydrogen generation is developed as an alternative way to produce H₂ starting from either conventional or renewable sources. The chemical-looping process can be performed using a number of different reductants, such

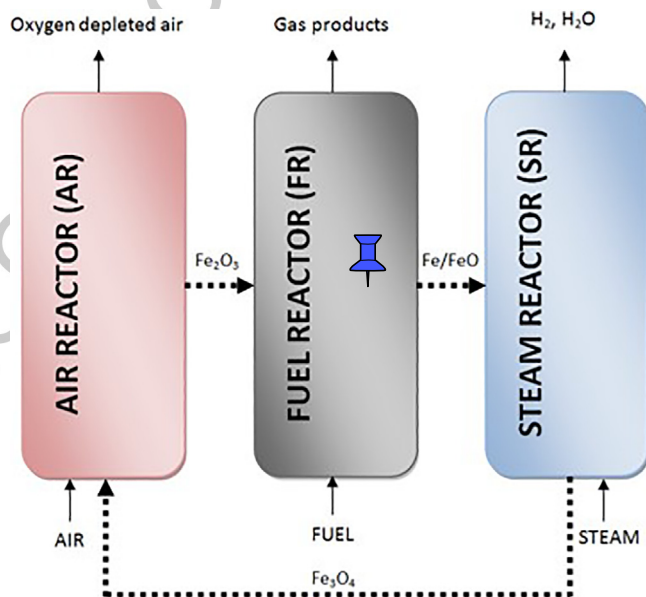
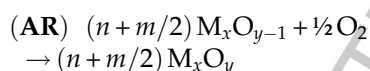


FIG. 14.6 Schematic representation of CLR for hydrogen generation over Fe-based oxygen carrier material.

p0220 A general statement can be made on the basis of the results obtained independently by several research groups: as the oxygen ratio in the system decreases, there is a higher tendency toward carbon formation, which in its turn leads to the lowering of the purity of the produced hydrogen. According to Cho et al. [57], the rate of carbon formation increased rapidly when more than 80% of the available oxygen in the Ni-based oxygen carrier was consumed. Galvita and Sundmacher reported that a maximum Fe reduction of 60% largely minimized carbon formation and a high purity hydrogen stream (<20 ppm CO) could be obtained [58].

p0225 Usually, the difficulty to restore the original oxidation state of the oxygen carrier material by means of only water steam can lead to the necessity of an additional oxidation step, like an air treatment:



p0230 Oxygen carrier material ($M_x O_y$), in its fully oxidized form, is further re-circulated to the fuel reactor (FR) for subsequent cycles.

p0235 Important aspects for the overall effectiveness of the process lie in the choice of operation conditions, appropriate reactor designs (fluidized bed [59–61]/moving bed [62]/fixed bed [63–66] reactors), and identification of suitable candidates to be used as corresponding oxygen carrier materials.

s0100 5.1 Oxygen Carrier Materials

p0240 One of the key parameters that determines the overall efficiency of many chemical-looping processes for hydrogen production, lies in the selection of a suitable oxygen carrier material, taking into account several properties: reaction kinetics, thermodynamic feasibility of oxygen transfer, redox properties, oxygen content, stability and recyclability, high resistance to attrition,

heat capacity, melting points, tendency to form coke, resistance to coke formation and accumulation, low cost, toxicity, etc. [44]. Thus, many research groups focus their attention on the improvements of the activity and stability of the oxygen carrier material through optimization of its composition, screening of the supports along with the particle structure optimization. Ideally, appropriate oxygen carriers should have fairly high conversion rates in both reduction and re-oxidation reactions, high agglomeration/sintering resistance, maximum fuel conversion with minor carbon deposition, and be economically and environmentally friendly [67].

Reduction and oxidation reactions, which are the main prerequisite to any chemical-looping process, require additional information on the thermodynamic aspect of a suitable redox couple— $M_x O_y / M_x$, which determines the final effectiveness of the process with a choice of operating conditions. In the review, published by Fan et al. [11], a comparative thermodynamic assessment of different oxygen carrier materials was made based on modified Ellingham diagram, where metal oxide materials can be grouped into several zones, depending on their applications. For example, materials like $V_2 O_5 / V$, $CeO_2 / Ce_2 O_3$, WO_3 / W , or ZnO / Zn are capable to only partially oxidize the fuel, whereas NiO / Ni , $Fe_2 O_3 / FeO$, CuO / Cu , or $Co_3 O_4 / Co$ have strong oxidizing properties and foster total oxidation reactions. Thus, Ni, Fe, Co, and Cu metal oxides are often used as the main constituents of oxygen carrier materials for chemical-looping applications. A review published by Voitic et al. [46] covers data on the development of different oxygen carrier materials, and comprises studies on the naturally occurring and synthetically derived bulky or supported materials. In addition, a summary on the different oxygen carrier materials for the hydrogen production via chemical-looping processes was published by

Protasova et al. [67]. The review encompasses information on the different perovskites and Ni/Fe/Cu/Ce-based oxygen carrier materials. Perovskites showed good results for the partial oxidation of methane. With Fe-based materials, promising results have also been obtained (they are considered replacements for Ni-based oxygen carriers because of their lower price and toxicity). Many studies were performed by testing different active metal component, namely, Fe, W, Sn, Ni, Cu, Mn, and Ce. However, more recent works were almost exceptionally focused on iron-based oxygen carriers combined with several inert components aimed to improve their mechanical and chemical properties. Several research groups have been exploring modifications of simple iron oxide (Fe_3O_4 and Fe_2O_3) in order to prevent deactivation [68], lowering of the operating temperature [69] and increase of the structural stability and reducibility [70,71], the reaction rate for oxidation, and the total efficiency of the process [72,73]. Several studies were dedicated to different metal additives to iron oxide [74,75]. In addition, ternary metal systems have also been considered in the search for a better synergetic effect [76,77]. Several research groups have investigated the effect of various M-additives on the stability and redox behavior of iron oxide for chemical hydrogen storage using Pd, Pt, Rh, Ru, Al, Ce, Ti, Zr [78] and Al, Cr, Zr, Ga, V, Mo [79]. And it was found out that Pd, Pt, Rh, and Ru additives have an effect on promoting the reduction and lowering the re-oxidation temperature of iron oxide. At the same time, Al, Ce, Ti, Zr, Cr, Ga, and V additives prevent deactivation and sintering of iron oxide during repeated redox cycles. Some recent studies on developing novel and efficient oxygen carrier materials for chemical-loop applications highlight the special interest of spinel oxides [18,26,68,69,72,73,80–90], which can be explained by their thermodynamic stability, which allows them to re-obtain the initial oxidized spinel phase upon redox cycling and increase the stability of the looping material.

5.2 Spinel Oxides as Oxygen Carrier Materials

s0105

Spinel oxides with a generic formula of AB_2O_4 are chemically and thermally stable materials suitable for various applications including catalysis. From a chemical aspect, spinels exhibit acid-base and redox properties, which play a key role in several catalytic reactions involving oxygen species [49]. Moreover, according to the nature of incorporated cations, they can host a variety of redox couples (e.g., Fe(II)/Fe(III), Mn(II)/Mn(III), or Co(II)/Co(III)), which make them suitable materials for Chemical-Looping applications [91]. As a confirmation, several studies of different M-modified (M = Ni, Co, Cu, Mn) iron oxides of the spinel family have shown that the redox properties of these materials render them effective electrons and O^{2-} vectors for the production of hydrogen via chemical-loop reforming (CLR) of alcohols (mainly C_1 – C_2 light alcohols) [48–56] (see Table 14.1, Scheme 14.1).

p0250

5.3 Spinel Oxides for Methanol Chemical-Loop Reforming

s0110

CoFe_2O_4 spinel oxide was applied as an oxygen carrier material in a two-step chemical-loop reforming process using methanol as a reductant [48,50]. The study performed by Crocellà et al. [48] revealed an evident correlation between physicochemical and catalytic properties of the looping material. Particularly, CoFe_2O_4 spinel was calcined at 450°C and 750°C (CF450 and CF750, respectively) in order to evaluate an effect of different morphological features as crystallite-particle sizes on the methanol decomposition and a stepwise reduction of the solid. It was shown that surface octahedral sites ($\text{Co}^{2+}/\text{Fe}^{3+}$) are the most reactive species, and are present in a higher amount on the CoFe_2O_4 sample calcined at a lower temperature (namely, 450°C). However, it was demonstrated that two spinel oxides, initially rather different from one another, exhibited similar features after just

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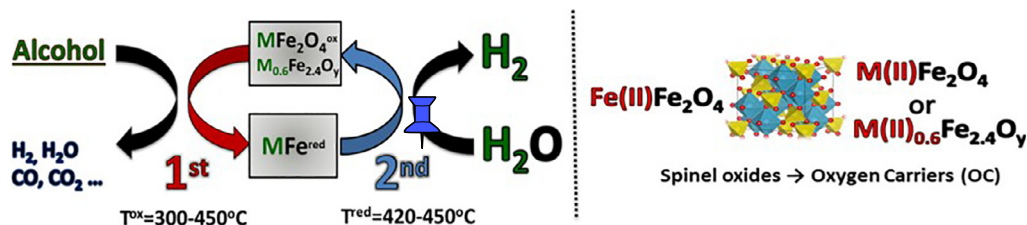
TABLE 14.1 Summarized Data on Spinel Oxides as Oxygen Carriers for Chemical-Looping Applications

Reductant	Oxidant	T_{red} (°C)	T_{ox} (°C)	Oxygen Carrier	Reduction Degree (%)	Ref.
CH ₃ OH	H ₂ O	300	420	(a) CoFe ₂ O ₄ (CF450)	(a) 100 ^{T(300)}	Crocella [48]
		420		(b) CoFe ₂ O ₄ (CF750)	(b) 82 ^{T(300)}	
CH ₃ OH	H ₂ O	(a,b) 300	420 ^{H₂O}	(a) CoFe ₂ O ₄ (CF450)	(a) 100 ^{T(300)}	Cocchi [50]
	Air	(a) 420	450 ^{AIR}	(b) CoFe ₂ O ₄ (CF750)	(a) 100 ^{T(420)} (b) 82 ^{T(300)}	
C ₂ H ₅ OH	H ₂ O	–	–	(a) CoFe ₂ O ₄ (CF450)	–	Velasquez Ochoa [56]
				(b) Fe ₃ O ₄ (FF450)		
				(c) NiFe ₂ O ₄ (NF450)		
C ₂ H ₅ OH	H ₂ O	450	450	(a) Fe ₃ O ₄ (FF450)	(a) 57	Trevisanut [53]
				(b) NiFe ₂ O ₄ (NF450)	(b) 69	
C ₂ H ₅ OH	H ₂ O	450	450	Fe ₃ O ₄	–	Trevisanut [55]
C ₂ H ₅ OH	H ₂ O	450	450	(a) CoFe ₂ O ₄	(a) 78	Trevisanut [52]
				(b) Fe ₃ O ₄	(b) 29	
				(c) NiFe ₂ O ₄	(c) 52	
				(d) CuFe ₂ O ₄	(d) 53	
C ₂ H ₅ OH	H ₂ O	450	450	(a) Co _{0.6} Fe _{2.4} O _y	(a) 98	Vozniuk [54]
				(b) Co _{0.54} Mn _{0.06} Fe _{2.4} O _y	(b) 100	
				(c) Co _{0.3} Mn _{0.3} Fe _{2.4} O _y	(c) 32	
				(d) Mn _{0.6} Fe _{2.4} O _y	(d) 19	
C ₂ H ₅ OH	H ₂ O	450	450	(a) CoFe ₂ O ₄	(a) 82	Vozniuk [51]
				(b) Cu _{0.5} Co _{0.5} Fe ₂ O ₄	(b) 100	
				(c) CuFe ₂ O ₄	(c) 82	
				(d) Cu _{0.5} Mn _{0.5} Fe ₂ O ₄	(d) 73	
				(e) Co _{0.5} Mn _{0.5} Fe ₂ O ₄	(e) 10	
				(f) MnFe ₂ O ₄	(f) 8	
C ₂ H ₅ OH	H ₂ O	450	450	(a) CoFe ₂ O ₄	–	Carraro and Vozniuk [49]
		350		(b) FeCo ₂ O ₄		

one reduction/re-oxidation cycle, where the surface properties of CF450 and CF750 were irreversibly modified. Reduction of the solids was performed at 300°C and 420°C and, based on

the product's distribution, different reaction zones (I–IV) were distinguished. Thus, during the early stage of the reduction, methanol conversion reached 19% and CO, CO₂, and H₂

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sch0010 SCHEME 14.1 Chemical-loop reforming of alcohols with spinel oxides as oxygen carriers.

(with small amount of CH_4 , H_2O and other oxygenates) were detected as initially formed products. With increasing the reduction time (specifically, solid exposure to the reactants stream), coke and CO_2 were produced in a higher amount, whereas methanol conversion and the solid reduction reached their maximum ($X = 88\%$ and $\alpha = 100^{\text{CF450}}/82^{\text{CF750}}\%$, where X = conversion and α = degree of reduction). Further research on the CoFe_2O_4 as a looping material was performed by Cocchi et al. [50]. It was confirmed that the reduction degree of the solid, together with the temperature at which reduction was carried out, significantly affected the methanol conversion and product's distribution. A higher reduction temperature (420°C) led to an increase of the solid reduction rate, despite all occurred phenomena were similar to those observed at 300°C . Moreover, it was found that a complete recovery of the initial oxidation state of Co-ferrites was not possible using only H_2O as an oxidant and a third step with air was added. The material obtained after the three-step CLR process showed quite similar reactivity results to that of the freshly calcined CoFe_2O_4 samples. This indicates that a complete restoration of the spinel phase was possible even after the formation of both metallic species and Fe carbide compounds during the first reduction step.

s0115 5.4 Spinel Oxides for Ethanol Chemical-Loop Reforming

p0260 Based on the two steps discussed, the chemical-looping reforming process, in which different M-modified spinel oxides were used

as oxygen carrier materials, Trevisanut et al. [52,53,55] investigated ethanol as a reducing agent. The choice of ethanol as a reducing agent has several advantages, including its renewable origin, and the possibility to decompose at a relatively lower temperature with the formation of a hydrogen-rich mixture [54]. A study performed on a bare Fe_3O_4 sample [55] showed that magnetite during the reduction step tends to form Fe^0 which is then converted to Fe_3C (cementite). However, the formed carbide can decompose to metallic iron and carbon ($\text{Fe}_3\text{C} \rightarrow 3\text{Fe}^0 + \text{C}$) and, similarly, catalyze growth of graphitic filaments and increase the rate of coke deposition. In order to reduce formation and accumulation of coke during several consecutive redox cycles, it was proposed to apply a short time on-stream approach (with reduction time of 5 min), because the formation of cementite was slightly delayed at the beginning of the reduction step. Reducibility of magnetite was improved by incorporation of several transition metals like Co, Cu, and Ni into the spinel structure [52,53]. Eventually, coke formation remained an issue for M-modified ferrosinels, which means that to avoid a completely carbon deposition and its further accumulation is not possible. Nevertheless, the best-performing material amongst tested oxygen carriers was CoFe_2O_4 , which underwent the greatest extent of reduction and was able to maintain it throughout several repeated cycles [52].

Velasquez Ochoa et al. [56] studied the reduction mechanism of M-modified (Ni, Co, and Fe) spinel oxides, where ethanol was the reductant.

p0265

It was concluded that the first step in ethanol anaerobic decomposition appears to be the same for all samples and corresponds to acetaldehyde formation via dehydrogenation of ethanol. Further reduction of the solid was strongly dependent on the nature of incorporated M (Ni, Co, or Fe), specifically, acetaldehyde can be either oxidized to acetates (NiFe_2O_4), decomposed to CO and CH_4 (CoFe_2O_4), or completely oxidized (Fe_3O_4). Vozniuk et al. investigated binary and ternary mixed-spinel oxides ($\text{M}_x^1\text{M}_{0.6-x}^2\text{Fe}_{2.4}\text{O}_y$ and $\text{M}_x^1\text{M}_{1-x}^2\text{Fe}_2\text{O}_4$, where M=Co, Mn, Cu) as oxygen carrier materials in two-step CLR of ethanol. It was observed that the incorporation of Mn/Co metal cations into Fe_3O_4 crystal structure affects the reducibility of the resulting spinels (Fe-rich ferromagnetic: $\text{M}_x^1\text{M}_{0.6-x}^2\text{Fe}_{2.4}\text{O}_y$). Co incorporation was found to enhance reactivity in the anaerobic decomposition/oxidation of ethanol, whereas Mn incorporation significantly reduced the coke formation during the first reduction step [54]. Consecutive studies on the $\text{M}_x^1\text{M}_{1-x}^2\text{Fe}_2\text{O}_4$ as oxygen carriers revealed that Co/Cu-incorporation facilitates total/partial oxidation of ethanol giving rise to high yields of H_2 , CO_x , and H_2O , whereas Mn-incorporation predominantly favored dehydrogenation and condensation reactions leading to the formation of acetaldehyde and acetone. Besides, the incorporation of Mn contributed to significantly reduce the amount of coke that was attributed to the formation of a thermodynamically stable and hardly reducible layer of $\text{Mn}_x\text{Fe}_y\text{O}$ solid solution [51]. A study on CoFe_2O_4 and FeCo_2O_4 as oxygen carrier materials was performed by Carraro et al. [49]. During the reduction step with ethanol, FeCo_2O_4 was reduced faster compared with CoFe_2O_4 . However, its performance during the re-oxidation step is quite poor due to an inefficient oxidation by water steam, which is able to oxidize only the outer shell of the nanoparticles, resulting in small H_2 yield [49]. On the other hand, the CoFe_2O_4 sample was a more efficient oxygen carrier, which enables it to produce larger amounts of H_2 due to the

residual presence of a reducible wüstite, which can be consecutively re-oxidized/reduced in further looping cycles.

5.5 Summary on Spinel Oxides as Oxygen Carrier Materials s0120

A variety of studies have been performed on ferromagnetic spinels of different compositions (MFe_2O_4 and $\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y$, where M=Fe, Ni, Cu, Co, and Mn), whereby the following general statements can be made: p0270

1. The incorporation of transition metals, such as Ni, Cu, Co, and Mn (or their combinations Cu/Co, Co/Mn, Cu/Mn), strongly affects final redox properties of the resulting materials. Overall, the reducibility of magnetite (Fe_3O_4) is enhanced with the introduction of secondary metals (Co, Ni, and Cu) into the spinel structure. Besides, its presence in a smaller amount (as in $\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y$ type materials, with Fe:M ratio of 4:1) is already sufficient to observe positive results on the production of H_2 via a two-step chemical-looping reforming process compared with nonmodified Fe_3O_4 . o0045
2. The incorporation of Mn contributed to significantly reducing the amount of coke formed, however, it caused a lower intrinsic reducibility which was explained by the formation of a thermodynamically stable and hardly reducible layer of $\text{Mn}_x\text{Fe}_y\text{O}$ solid solution. It is important to note that the final purity of hydrogen is limited by the coke which is formed during the reduction step. As mentioned earlier, this problem can be partially overcome by changing the spinel composition, or shortening the overall time of the redox cycles to 5 or 20 min (time accounts to the total time of reduction/re-oxidation step) (note: the problem of an impure stream can also be overcome by the utilization of a three-step CLR process with the third step being carried out with air [92]). o0050

p0285 Nonetheless, another challenge needs to be tackled in the future; with each performed cycle the material tends to deactivate as the result of:

- o0055 1. Deep modification of the starting material via sintering and segregation phenomena,
- o0060 2. Continuous or sequential “coking” of the material with each performed cycle due to the impossibility to achieve a total removal in the conventional CLR process,
- o0065 3. Incomplete re-oxidation of the metallic component (M^0) using just H_2O as an oxidant.

p0305 On the other hand, modifying the conventional two-step process by adding the third step with air helped to overcome these problems, and is a first approach to overcome the above-described limitations [92]. As a general conclusion, it needs to be underlined that the chemical-looping reforming (CLR) process remains a very attractive target for researchers and industry in particular, and the future global energy economy in general. Many efforts to reach this goal have been undertaken and are reviewed herein. From the discovery the CLR process went to pilot plant stage but never managed to truly become economically viable. The future focus of researchers needs to be steered toward the current shortcomings of the process. Despite that several improved looping materials have been proposed, nonsintering and noncoking catalysts need to be conceived. Moreover, complete appraisals of their performance and further optimization studies are required in order to give information on the overall conversion efficiencies, process design, and economics.

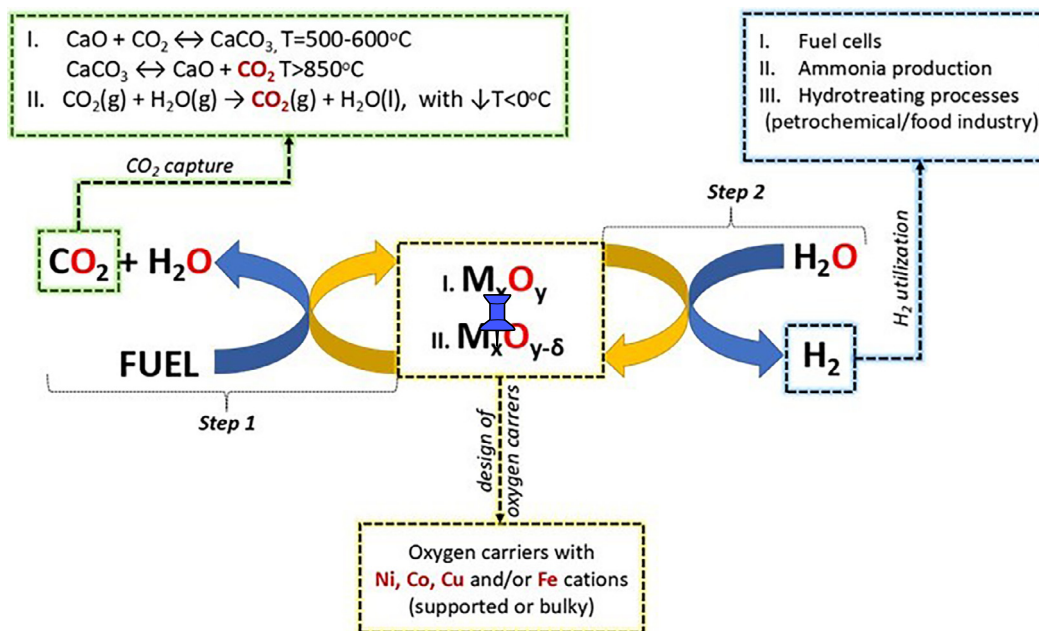
s0125 6 CONCLUSIONS

p0310 Interest in hydrogen, as an energy carrier, has been extensively growing in recent decades, which is powered by its environmental advantages over classical energy sources such as natural gas and coal. At this point, the future perspective of a hydrogen economy has triggered

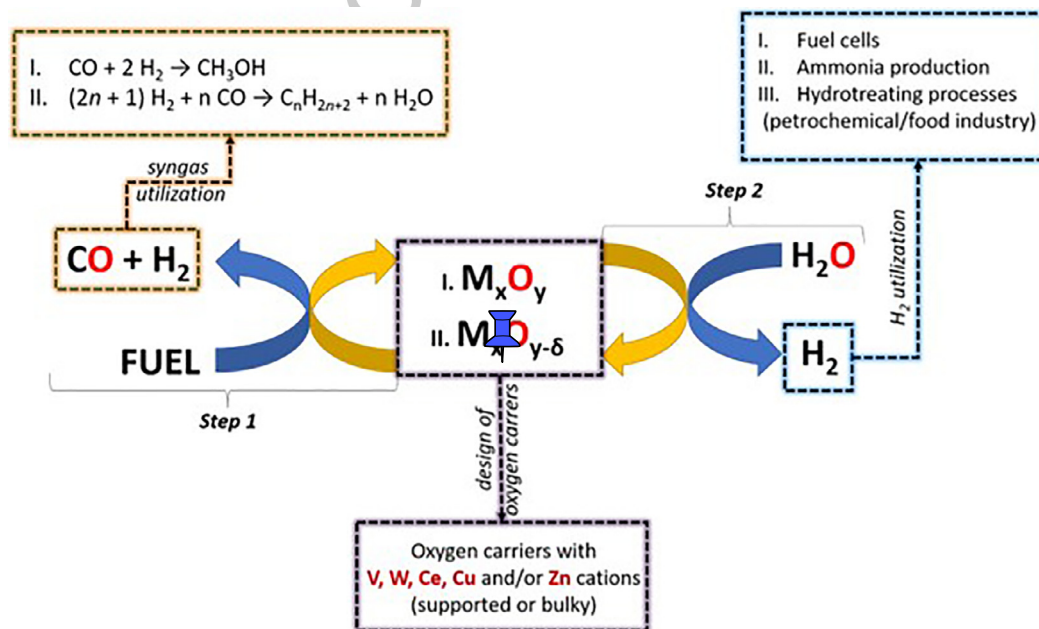
many researchers to develop and optimize a series of new technologies which differ from conventional industrial processes (like SMR, ATR, POX, and H_2O -electrolysis) in their orientation toward minimization of emission of greenhouse gases (on-site CO_2 capture), utilization of renewable feedstock (bio-alcohols, bio-gases, wood, and algae), or renewable energy sources (wind, sunlight, or tides).

One of the new technologies, which is aimed p0315 to produce hydrogen in a more sustainable manner, is chemical-looping hydrogen or chemical-looping water splitting process. Initially, the chemical-looping concept was oriented on the combustion of different fuel feedstocks to generate heat and power, called the chemical-loop combustion process; only later it was applied to the generation of hydrogen. Over the last decades, this approach has been extensively investigated by many research groups, and more than 100 chemical-looping cycles with different operating parameters, engineering challenges, and hydrogen production opportunities are described in the literature. Ideally, the chemical-looping process is aimed to produce high purity hydrogen without any additional separation steps that are the issues of today’s industrial processes. Eventually, this technology may offer several other opportunities for process intensification through selection of the oxygen carrier materials and design of the reaction paths which can be either partial or total oxidation of the fuel, generating a variety of products ranging from syngas and hydrogen to olefins and liquid fuels (Schemes 14.2–14.4). Summary schemes indicates that hydrogen remains to be a target product, however, overall efficiency of the chemical-loop processes can be maximized by converting reducing fuels into valuable products (Schemes 14.3 and 14.4).

Several chemical-looping pilot and sub-pilot p0320 plants [93–95] went on stream but have not been successfully demonstrated commercially to the date. The main reason deals with oxygen carrier materials, namely, their insufficiency in

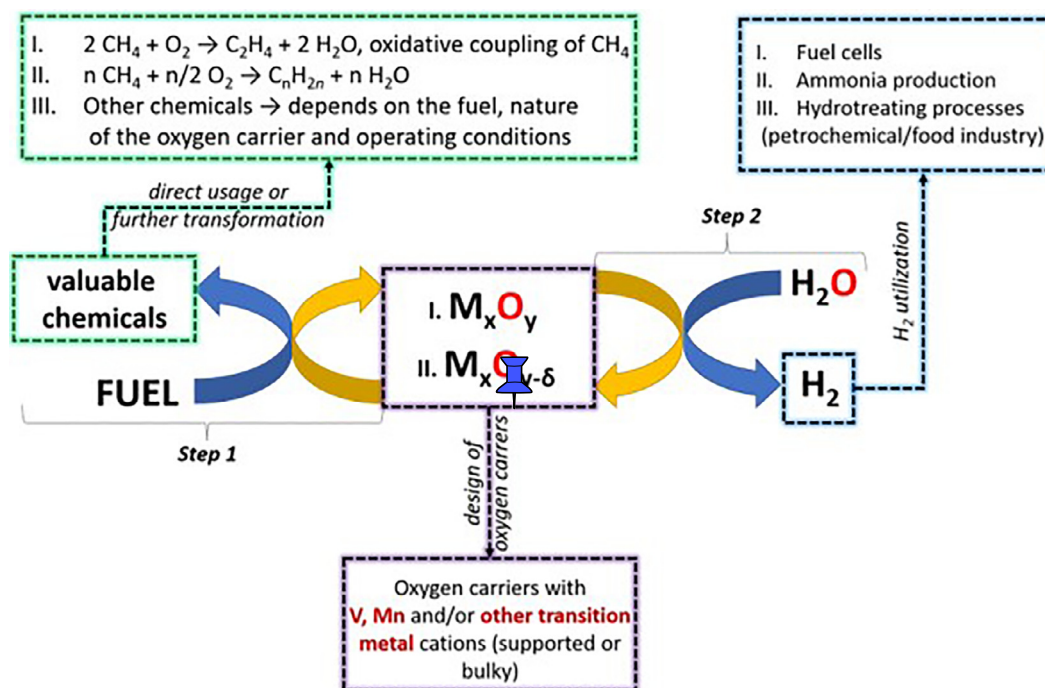


Q20 sch0015 SCHEME 14.2 Hydrogen production with inherent on-site CO₂ capture and separation.



Q21 sch0020 SCHEME 14.3 Hydrogen production with on-site simultaneous syngas generation.

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sch0025 SCHEME 14.4 Hydrogen production with on-site simultaneous co-production of other chemicals.

reactivity, stability and recyclability, physical strength and attrition resistance, tendency to form and accumulate coke, and oxygen-carrying capacity. Another reason is linked to the reactors design and solid circulatory systems, specifically the lack of design know-how on high-solid loading flows, nonmechanical devices, and gas-solid reactors for achieving high oxygen-carrier conversions [11]. Despite the remaining challenges, ongoing research in this field brings new solutions to the existing limitations, which gives a potential to the chemical-looping technology.

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Non-Print Items

Abstract

Interest in hydrogen as a possible energy vector is powered by the depletion of fossil fuel feedstocks as well as concerns over global warming, which brings new environmental legislations on the emission of greenhouse gases into the atmosphere. At this point, the future perspective of a hydrogen economy has triggered many researchers to develop and optimize a series of new technologies which differ from conventional industrial processes (like SMR, ATR, POX, and H₂O-electrolysis) in their orientation toward the minimization of emission of greenhouse gases (on-site CO₂ capture), utilization of renewable feedstock (bio-alcohols, bio-gases, wood, and algae), or renewable energy sources (wind, sunlight, or tides). This chapter gathers information on the most relevant technologies for hydrogen production, including discussions on existing conventional reforming processes, as well as developments in advanced and more environmentally benign methods, like chemical-looping.

Keywords: Hydrogen, Water splitting, Chemical looping, Alcohol reforming, Oxygen carriers, Spinel oxides, Ferrites

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