Ceria-Based Materials for Hydrogen Production Via Hydrocarbon Steam Reforming and Water-Gas Shift Reactions

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Abstract: This review paper provides an overview of the use of ceria-based catalytic materials towards the industrial hydrogen production via the hydrocarbon steam reforming and the water-gas shift reaction routes with a focus on representative patenting activities mainly in the last 10 years. We first introduce the basic mechanisms of catalytic hydrocarbon steam reforming and conversion of carbon monoxide by steam towards a mixture of carbon dioxide and hydrogen at low and high temperatures, the main synthetic approaches of ceria material and its basic structural properties responsible for its catalytic activity exhibited towards the present reactions. In the case of hydrocarbon steam reforming, emphasis is given on the (i) sulphur tolerance of catalysts developed, (ii) efforts to reduce the reaction temperature, (iii) use of the “Absorption Enhanced Reforming” concept, and (iv) its application in fuel cells for power generation. In the case of water-gas shift reaction, progress in catalyst developments for low- and high- temperature applications is discussed. Future directions in these fields have been suggested.

Keywords: Hydrogen production, CeO₂-based catalysts, steam reforming of hydrocarbons, water-gas shift, WGS, auto-thermal reforming, ATR, absorption enhanced reforming, AER, fuel cell.

1. INTRODUCTION

Steam reforming of natural gas and other hydrocarbons is the least expensive and widely used industrial process of hydrogen gas production largely required for the manufacture of ammonia and methanol, hydro-treatments of petroleum fractions, and production of C₅-C₁₂ hydrocarbons (gasoline fraction) by the Fischer-Tropsch process. Steam reforming is a multi-step endothermic process and currently satisfies 90-95% of the world’s needs for hydrogen production (Fig. (1)) [1]. In the case of use of solid fuel as a feedstock (Fig. (1)), coal is the conventional one used today, where carbon gasification is performed via the use of steam, while part of the coal is burned to form CO and CO₂ in order to supply heat for the coal gasification (endothermic reaction). The cost of hydrogen from steam reforming of methane (SRM) varies with feedstock cost and scale of production, and it is about 2-5 U.S. $ per kilogram [2]. The SRM process requires high temperatures and this is achieved through burning of natural gas [3]. In general, steam reforming of hydrocarbons is one of the widely applied catalytic processes leading to CO/H₂/CO₂ gas streams (“syngas”) of varying H₂/CO molar ratio depending on reaction conditions and catalyst composition used. More precisely, hydrocarbons in the presence of a solid catalyst react with water (steam) at elevated temperatures (endothermic process) and pressures towards the production of a gas mixture mainly consisting of H₂, CO, CO₂ and CH₄ (reformate). In this chemical process, a multi-step reaction network, a combination of steam reforming and water-gas shift reactions takes place as described below.

- In the first step, the hydrocarbon feedstock is purified by the removal of sulfur-containing compounds. This is accomplished by using hydro-desulfurization catalysts (e.g., Co-Mo or NiMoS) followed by absorption of H₂S over ZnO solids.

- In the second step, an endothermic reaction of hydrocarbon with steam in the 800-1000°C range and at a pressure around 30 bar occurs. A typical solid catalyst used is Ni metal supported on alumina, silica, magnesium or calcium aluminate, whereas the product stream mainly consists of H₂, CO, CO₂ and CH₄. In the case of SRM process, the following reaction occurs:

\[ CH₄ + H₂O \leftrightarrow CO + 3 H₂ (ΔH²⁰° = + 206kJ/mol) \]  

In general,

\[ CₙHₘ + m H₂O \leftrightarrow m CO + (m+1/2 n) H₂ (ΔH²⁰° > 0) \]  

where, ΔH²⁰° is the standard heat of hydrocarbon steam reforming reaction, which is hydrocarbon chemical composition dependent.

- In the third step, the carbon monoxide formed reacts with steam in the presence of a solid catalyst. This is the so-called water-gas shift (WGS) reaction and which results into the formation of carbon dioxide and further hydrogen production, as described by the following equation:

\[ CO + H₂O \leftrightarrow CO₂ + H₂ (ΔH²⁰° = -41.1kJ/mol) \]  

The WGS reaction is a very important step in the industrial processes of H₂, ammonia and methanol synthesis.
The catalysts used in the steam reforming of hydrocarbons processes can be divided into two groups: non-precious metals (usually nickel) and precious metals from Group VIII elements (typically platinum or rhodium). Rh-based catalysts are preferred since they exhibit higher specific activity than nickel catalysts [1, 12]. However, the high cost of Rh has motivated some researchers to develop Co-based catalysts [13]. Coke deposition on the surface of Ni-based catalysts is minimized when noble metal is used. In addition, promotors, such as magnesia or potassium, or other alkaline components are added into the support to enhance gasification of deposited carbon [14] and sustain catalytic activity with time on stream.

A general view of the mechanistic path followed during steam reforming reaction over a supported metal catalyst can be described as follows. The hydrocarbon molecule is adsorbed on the metal component (e.g., Pt, Rh, Ni, Pd) of the catalyst, where it undergoes successive dehydrogenation steps, (Fig. (2)). This leads to the formation of \( \text{C}_x\text{H}_y \) fragments and adsorbed H species. On the other hand, water \((\text{H}_2\text{O})\) molecules are adsorbed mainly onto the support and dissociate into H and \(-\text{OH}\) species, the former accommodated on support oxygen species to form additional \(-\text{OH}\) groups. These species diffuse from the support towards the metal-support interface (back-spillover process), where they react with the hydrocarbon fragments \( \text{C}_x\text{H}_y \) to form \( \text{H}_2 \), CO and \( \text{CO}_2 \) [15-17]. The rate of formation of \( \text{C}_x\text{H}_y \) fragments appears to be structure sensitive, thus dependent of the metal particle size. Water dissociation and diffusion rates of derived H and OH species depend also on the chemical nature of support [16, 17]. Some state-of-the-art catalytic supports such as alumina, silica or magnesia are not so
efficient in H\textsubscript{2}O dissociation, and therefore high temperatures are needed (>700°C) to dissociate H\textsubscript{2}O into H and OH species.

For the WGS reaction, two mechanistic paths have been proposed so far: the \textit{regenerative or redox} mechanism, and the \textit{associative} one as depicted in Fig. (3) \cite{18-23}. According to the redox mechanism, the WGS reaction proceeds via consecutive steps of reduction and reoxidation of the catalyst surface (Fig. (3A)) \cite{18}. The redox mechanism occurs mainly in high-temperature shift catalysts, where reducible metal oxide supports are used. The associative mechanism involves interaction between CO and H\textsubscript{2}O molecules on catalyst active sites to form surface intermediates (mainly formates) which further decompose to reaction products, CO\textsubscript{2} and H\textsubscript{2} with likely the participation of metal active phase (Fig. (3B)) \cite{19}. It has been proposed that WGS reaction proceeds at the boundary between small metal particles and the support in the case of supported metal catalysts \cite{19-23}.

The water-gas shift reaction is moderately exothermic, so the equilibrium constant ($K_p$) decreases with increasing temperature \cite{8}. In the 588-753K range, it is given by the following relationship:

$$K_p = \exp[(4577.8/T) - 4.33]$$

where T is in [K]. It is noted that very high equilibrium conversions are achieved at low-temperatures (T< 523K). Since the reaction is reversible, the rate of forward reaction is inhibited by the reaction products H\textsubscript{2} and CO\textsubscript{2}. In industrial practice, where close to adiabatic conditions are applied, the increase of reaction temperature leads to lower CO conversions due to thermodynamic limitations. This thermodynamic constrain is practically faced by using two or more catalytic beds, where heat is removed between them. In general, at the exit of the high-temperature reactor CO concentrations of 3-5 vol% are achieved, whereas at the exit of the low-temperature reactor the CO concentration drops to 0.3 vol%. WGS gas concentrations (CO, CO\textsubscript{2}, and H\textsubscript{2}) depend on reformer’s operation, and these are governed by thermodynamic equilibrium constrains.

### 2. STRUCTURAL PROPERTIES AND SYNTHETIC APPROACHES OF CeO\textsubscript{2}-BASED MATERIALS

#### 2.1. Structural Properties of Ceria

Ceria or cerium dioxide (CeO\textsubscript{2}) is a well known important component for the control of automotive emissions (“three-way” catalyst) and for other environmental and energy-related applications, primarily for its intrinsic property of oxygen storage; receiving oxygen under oxidizing gas conditions, and releasing oxygen under reducing gas conditions \cite{24-29}. CeO\textsubscript{2} plays a major role in steam and dry reforming of hydrocarbons, and the WGS catalytic reactions. For the WGS reaction, precious metals (e.g., Pt, Rh, Pd) are not oxidized easily by water. However, oxidation of Ce\textsubscript{2}O\textsubscript{3} (Ce\textsuperscript{IV}) by water is thermodynamically favorable. The reduction/oxidation behavior of CeO\textsubscript{2} is facilitated by the presence of dopants (ceria-doped materials) such as Zr\textsuperscript{4+}, La\textsuperscript{3+} and other rare-earth metal cations. In addition, heat resistance of CeO\textsubscript{2} is much improved by the introduction of Zr\textsuperscript{4+} or rare-earth metal cations in the ceria lattice \cite{30}. There are many patents claiming the improvement of ceria’s thermal stability by the addition of rare-earth elements and/or zirconium, mainly due to grain growth inhibition, thus maintaining the oxidation-reduction performance even at high temperatures \cite{31, 32}. In addition, CeO\textsubscript{2} has been reported to enhance the thermal stability of alumina \cite{33, 34}. In particular, US4714694 patent (Wan \textit{et al.} 1987) \cite{35} discloses aluminum to stabilize bulk ceria which is used as support for platinum group metal components. Use of ceria as support for noble metals other than Rh can be found in US4727052 (Wan \textit{et al.} 1988) \cite{36} and US4708946 patents (Ohata \textit{et al.} 1987) \cite{37}.

Details of the structural properties of ceria-based materials and their importance became first known through research conducted on automotive emission control, and since then these have been exploited in many other catalytic applications \cite{38}. For example, ceria can act as co-catalyst with a noble metal loaded on it, providing oxygen via diffusion through its lattice and on its surface towards the
noble metal surface, thus oxidizing carbon monoxide or hydrocarbons adsorbed and activated onto a supported metal surface [39].

The ceria-based mixed metal oxides were found to exhibit improved catalytic performance in comparison with pure ceria, mainly due to modifications of the fluorite-type lattice which are induced by the addition of a second metal cation. In the case of Zr$^{4+}$ substitution for Ce$^{3+}$ (1.01Å), the smaller Zr$^{4+}$ (0.86Å) cation causes a distortion in the fluorite crystal lattice, while oxygen ions appear to be more mobile (labile). In particular, after introducing Zr$^{4+}$ cations into the cubic CeO$_2$ lattice structure, Ce-O-Ce and Ce-O-Zr bond lengths in the Ce$_x$Zr$_{1-x}$O$_2$ lattice shorten, and coordination of the oxygen around Zr$^{4+}$ adopts a more centro-symmetric 8-fold coordination [40, 41]. This alteration in the oxygen local bonding environment around Ce$^{3+}$ and Zr$^{4+}$ cations results in the creation of active oxygen species that play a predominant role in the Oxygen Storage Capacity (OSC) property of ceria-based materials [42, 43], which is directly linked with the catalytic activity towards hydrocarbon steam reforming and water-gas shift reactions [20, 44]. Furthermore, the high density of defects in these types of nanostructured materials [37] provides a large number of active sites for ionic conduction and a high diffusion path via the nanometer-sized interface boundaries that promote fast kinetics. It is noteworthy that for CeO$_2$-based mixed metal oxides (e.g., Ce-Zr-O, Ce-Hf-O, Ce-La-O, etc.) it is desirable to maintain their cubic structure. The cubic structure is usually linked with greater oxygen mobility, and hence enhances catalytic activity. For example, Ce$_x$Zr$_{1-x}$O$_2$ compositions with 0.5 < x < 0.8 have shown the most promising results for oxygen storage capacity (OSC) and reduction properties [45]. Yashima et al. [46] reported that ceria presents tetragonal structure when zirconia concentration levels exceed 20 wt%. This occurs since oxygen anion lattice is distorted into a tetragonal phase, while the cerium and zirconium cations remain in a cubic lattice, forming a metastable pseudo-tetragonal phase lattice.

For the structural investigation of CeO$_2$-based mixed metal oxides, powder X-ray diffraction technique is employed. However, for ceria-zirconia with very small crystallite sizes, XRD pattern exhibits broad peaks. It is noteworthy that any tetragonal distortion caused by oxygen atoms due to doping is undetected in XRD, and thus the resulting diffractogram corresponds to a cubic structure. In such a case, Raman and EXAFS techniques are used to probe such phase transitions [41]. Zr$^{4+}$-doped CeO$_2$ exhibits structural and electronic modifications compared to pure CeO$_2$. Doping of Ce$_x$Zr$_{1-x}$O$_2$ solid solution with Zr$^{4+}$ affects the local chemical environment of oxygen atoms as evidenced by the oxygen K-edge XANES spectrum. For example, the band gap in Ce$_{0.8}$Zr$_{0.2}$O$_2$ is ~0.6eV smaller than in bulk CeO$_2$, with Zr$^{4+}$ to have smaller positive charges in the mixed metal oxide than the respective cations in ZrO$_2$ or CeO$_2$. Zr$^{4+}$ cations in the cubic CeO$_2$ lattice are forced to adopt larger metal-oxygen distances than in ZrO$_2$ resulting therefore in a decrease in the oxidation state of Zr cation [47].

Raman spectroscopy is an extremely valuable tool for assessing the extent of doping and effectiveness of CeO$_2$-based mixed metal oxides synthesis methods. A peak at 465cm$^{-1}$ is usually observed, which is assigned to the F2g vibrational mode characteristic of the cubic fluorite structure (Fm3m space group) [48]. For tetragonal ZrO$_2$, six raman active modes of Alg + 3Eg + 2B1g are observed (space group P4/nmc). Another very important feature is the appearance of peak at 580cm$^{-1}$ which is linked with lattice defects, resulting from the formation of oxygen vacancies. This peak is less prominent in the case of pure ceria, while it becomes stronger in the case of mixed metal oxides (e.g., Ce-Pr-O, Ce-Zr-O, etc.), which is attributed to the increase of oxygen vacancies concentration for charge compensation due to the presence of Pr$^{3+}$, and to the increased concentration of Ce$^{3+}$ cations. In the case of Ce$_x$Zr$_{1-x}$O$_2$ solid solution, a shift of Raman frequencies to higher values has been observed with increasing ZrO$_2$ content, mainly due to lattice shrinkage, leading to shorter M-O-M bonds [41].

UV-vis/DRS technique has been also proved to be a very valuable tool for studying various metal oxides to obtain information on bulk and surface coordination, and different oxidation states of the constituent ions due to d-d and f-d electronic transitions, and to estimate electronic band gaps due to oxygen-metal ion charge transfer [48]. For example, CeO$_2$ exhibits three absorption bands in the UV region, centered at ~ 255, 285 and 340nm. The first and second bands correspond to Ce$^{3+}$ → O$^2$ and Ce$^{4+}$ → O$^2$ charge transfer transitions, respectively, while the third band is associated with inter-band transitions [48]. It was reported that after Pr$^{3+}$ was added into the ceria lattice, the UV profile changed. In particular, an additional more intense absorption band in the 400-650nm region appeared which is linked to Pr$^{3+}$ ion transitions. Ce-Pr-O mixed metal oxide exhibits a blue-shift of the absorption edge as compared to pure ceria. This is attributed to the presence of Pr$^{3+}$ ions which stimulate an increase in the concentration of Ce$^{3+}$ ions, thus leading to an increase in the electronic gap between the O 2p and Ce 4f orbitals, and finally inducing the above mentioned blue shift in the absorption edge. These results indicate the existence of oxygen vacancy defects.

2.2. Synthetic Approaches

Many different synthetic approaches have been used to produce ceria-zirconia solid powders, namely: (i) co-precipitation, (ii) homogeneous co-precipitation, (iii) citrate process, and (iv) different sol-gel techniques [49]. The surface area of the mixed metal oxides obtained from the above mentioned techniques usually does not exceed 150m²/g. Wet chemistry approaches are preferable since they allow the formation of metastable phases along with the control of surface area, pore structure, and primary crystal size. Some other synthesis methods, such as the surfactant-assisted one have been reported to result in higher surface area (ca. 235m²/g) ceria materials [50]. However, this technique requires a lengthy aging time (ca. 90h), whereas removal of surfactant requires many cycles of washing with water. It is pointed out that the preparation method applied is very important for the final properties of CeO$_2$-based mixed metal oxides, namely: (i) surface area, (ii) morphology, (iii) thermal stability, and (iv) oxygen storage capacity. Many patents report on the impact of CeO$_2$ synthesis method on its structural properties and performance. Specific patents
claiming of methods for preparing thermally stable metal oxides can be found [51]. In particular, patents on different preparation methods, such as spray evaporation, US5762894 patent (Takatori et al. 1998) [52], ball milling and precipitation, US5571492 patent (Yao et al. 1996) [53], precipitation using cerous alkali metal sulfate double salt, US6150299 patent (Umemoto et al. 2000) [54], sol-gel with various raw materials, US5837642 patent (Tanaka et al. 1998) [55], and template-assisted methods, US6139814 patent (Shigapov et al. 2000) [51] have been reported.

Beyond the synthesis method adopted for the CeO2-based mixed metal oxides, a number of methods have been disclosed for improving fundamental characteristics of the ceria-zirconia mixed metal oxides, such as specific surface area and redox behavior [56-58], US7166263 patent (Vanderspurt et al. 2007) [59] relates to a ceria-based mixed metal oxide with a high surface area and small primary crystal size. Another contribution of this invention relates to the selection of the specific metal cations used as second metal (Hf, Zr), and to the method applied for making such kind of mixed metal oxides.

Supported metal catalysts are widely used in chemical industry, where a transition metal being the active component is dispersed on high surface area carriers, such as inorganic metal oxides. Recognizing the unique and unusual properties of such a system, US5993762 patent (Rajaram et al. 1999) [60] reported on a method of using a catalyst containing noble metal (Pt, Pd, Rh and Au) and cerium dioxides. This is a typical catalyst which favours CO oxidation towards CO2, a reaction step of significance in the WGS and steam reforming of hydrocarbons reactions, and in the automotive emission control. The breakthrough of this invention is that it provides a catalyst where noble metal particles are uniformly dispersed over a metal oxide surface, and without any hydrogen reduction pre-treatment the formation of anionic vacancies on the metal oxide is facilitated. It should be recalled here that oxide support greatly influences the catalytic properties of the metal, particularly in the case where strong metal support interactions (SMSI) occur.

The most recent synthetic approach to produce a hydrocarbon reforming catalyst is enclosed in US20100159297 patent (Lee et al. 2010) [61]. The catalyst includes a nickel active catalyst layer, a metal oxide (among manganese oxide, tin oxide, cerium oxide, rhenium oxide, molybdenum oxide and tungsten oxide), and an oxide carrier (among Al2O3, SiO2, ZrO2, TiO2, and yttria-stabilized zirconia). As shown in Fig. (4), the nickel active catalyst layer is supported on the oxide carrier, and the metal oxide is distributed on the nickel active catalyst layer. However, a coking site at which carbon is deposited during a reforming reaction may be formed on the surface of the nickel active catalyst layer. The inventors reported that the mixture of the metal oxide and nickel suppress the formation of a coking site in the nickel active catalyst. The method includes simultaneously loading a nickel precursor and a metal oxide precursor on an oxide carrier, and heat-treating the resultant. When the nickel and the metal oxide precursors are simultaneously loaded, via, for example, wet impregnation, an oxide carrier is uniformly mixed with a solution including both the nickel and the metal oxide precursors, and then the resultant is dried. The inventor tested the prepared catalyst for steam reforming of propane and n-butane and found to have excellent coking resistance.

3. HYDROGEN PRODUCTION VIA HYDROCARBON STEAM REFORMING OVER CeO2-BASED MATERIALS

3.1. Steam Reforming of Hydrocarbons (CxHy)

**Sulphur Tolerance**

There is a considerable number of patents published dealing with steam reforming of hydrocarbons (CxHy) over supported metal catalysts. However, one disadvantage of the current industrially used catalyst compositions is the lack of sufficient tolerance towards sulphur-containing compounds, which makes desulphurization of hydrocarbon feedstock at a level of less than 0.5ppm necessary, a process step which increases the cost of hydrogen production.

A sulphur tolerant catalyst consisting of an active catalytic phase, a support and a chemical promoter was presented in US6238816 patent (Cable et al. 2001) [62] towards diesel steam reforming. Active phase includes: Ag, Co, Cu, Fe, Pd and Pt metals. Among the supports, ceria, mullite and zirconia were studied, whereas chemical promoters such as Bi, Ca, La and Mg were claimed. The breakthrough of the patent was that the invented catalyst was found to be stable for up to 500h on stream in the presence of 0.3 wt% sulphur in the feed.

More active, sulphur and aromatic compounds tolerant supported metal catalyst compositions are claimed in US20040166056 patent (Eyman et al. 2004) [63]. The catalysts have the main chemical composition of M-XO2-YO2/Al2O3, where M is a transition metal selected among the group of Ni, Pt, Pd, Ru and Rh, X is a redox active metal oxide, such as MnO2, V2O5 and CeO2, Y is a redox inactive metal oxide such as TiO2 and ZrO2. As inventors claimed, the supported-Ni catalysts are very attractive from the economical point of view. Moreover, the CeO2-containing catalyst was tested for iso-octane steam reforming, where the S-content in the feed was varied in the 5-100ppm range and the hydrogen production was found to be in the 60-80 vol% range.
A supported metal catalyst with improved sulphur tolerance was developed and reported in US20040102315 patent (Bailie et al. 2004) [64]. In particular, the catalysts disclosed were 2%Rh-Li/30%CeO$_2$-ZrO$_2$/SiO$_2$-Al$_2$O$_3$ and 2%Rh-Li/40%CeO$_2$-ZrO$_2$/SiO$_2$-Al$_2$O$_3$ and compared with the 2%Rh-Li/30%CeO$_2$-ZrO$_2$/Al$_2$O$_3$ catalyst composition. In all cases investigated, Rh:Li ratio was kept to 10:1 molar. The catalytic performance of the materials was tested using gasoline feedstock containing 10ppm (low level) and 100ppm (high level) sulphur. Improved sulphur tolerance was found in the case of CeO$_2$-ZrO$_2$/SiO$_2$-Al$_2$O$_3$ support compared to CeO$_2$-ZrO$_2$/Al$_2$O$_3$. Also, in the case of low-sulphur content in the feedstock no effect on the catalytic performance was found, whereas in the case of high-sulphur content catalyst deactivation did occur at 973K but the concentration of non methane hydrocarbons (NMHC) was low. The durability of the catalyst performance for 120h on stream was tested in the absence of sulphur and it was found to be constant. This behaviour was attributed to the better coke resistance of the invented catalyst.

A porous carrier for steam reforming of hydrocarbons applications consisting of a composite oxide containing at least Al and Mg with a surface area of 10-300m$^2$/g was disclosed in US20070167323 patent (Kobayashi 2007) [65]. According to the inventor, this carrier exhibits excellent sulphur resistance up to 50ppm sulphur in the feed and can be produced massively. It is known that introduction in the feedstock of large concentrations of S-containing compounds causes deterioration of catalytic activity due to catalyst chemical poisoning. In such a case, an increased amount of desulfurization catalyst is needed, thus increasing the total cost of the process. Other patents have also reported on the development of sulphur resistant catalysts [66, 67].

Recently, Inui et al. [68] claimed the invention of a multi-component catalyst containing 0.5-15% Ni, 0.5-10% CeO$_2$, 0.5-5% La$_2$O$_3$, 0.1-2% Pt, 0.5-3% ZrO$_2$, 0.1-2% Re, and 0.1-2% Rh for thermo-neutral reforming of liquid hydrocarbon fuels. The catalysts of this invention exhibited dual functionality enhancing both combustion and steam reforming. The hydrogen conversion exhibited by this system was up to 97%, whereas no catalyst deactivation was observed. The process related to this invention could be used to produce hydrogen-rich gas from low-sulfur middle distillate petroleum fractions (e.g., heavy naphtha, kerosene, diesel), as well as light petroleum fractions, such as light naphtha. However, the inventors claimed that the catalyst can reform feedstocks containing less than 2000ppm of sulfur.

**Lowering the Temperature of Hydrocarbon Steam Reforming**

It is more than obvious that an industrial endothermic reaction process should be carried out at the lowest possible reaction temperature. In the present examined industrial catalytic process, a suitable catalyst composition with favorable kinetics for steam reforming and water-gas shift reactions at low-temperatures (e.g., less than 973K) and at the same time of sustainable long-term activity is required.

Alumina-supported metal catalysts are among the most developed ones for the steam reforming of hydrocarbons. Igarashi [69] has invented a catalytic system which comprises an alumina carrier and Ni as an active component, whereas metallic silver and at least one of the yttrium, cerium, praseodymium, lanthanum and samarium oxide as co-catalyst is required. Alumina-supported catalysts suffer from low-activity at temperatures lower than 773K, whereas at temperatures higher than 773K the surface area is reduced and the mechanical strength of the catalyst deteriorates. Also, the inventor has found that Rh/ZrO$_2$ catalyst is an effective catalyst for steam reforming at low-temperatures, but this catalytic system due to short life-time and insufficient activity cannot be used in industrial practice. In the same US5130114 patent (Igarashi 1992) [69] the inventor reported improved catalyst formulations for steam reforming of hydrocarbons, namely a Ru/ZrO$_2$ solid (catalyst a). Also, Rh or Ru supported on ZrO$_2$, where one element selected from the group of Ni, La, Pr, Nd, Sm, Th, U, Cr, Mg, Ca and Y was added as co-catalyst (catalyst b), and Rh or Ru supported on partially stabilized ZrO$_2$ are reported (catalyst c). For ZrO$_2$ stabilization different oxides, such as MgO, Y$_2$O$_3$ and CeO$_2$ were used. For the evaluation of the catalytic performance of these solids, different hydrocarbons such as methane, ethane, propane, butane, pentane, hexane, heptanes, octane, nonane, decane, cyclohexane, methlycyclohexane, and cyclooctane were tested. These hydrocarbons were used alone or in combination with two or more other co-fed hydrocarbons. The reaction temperature, S/C ratio, and GHSV were varied in the 673-1123K, 3-8, and 2,000-20,000h$^{-1}$ range, respectively. Among the different catalytic formulations investigated, Rh/12%CeO$_2$-ZrO$_2$ exhibited a total hydrogen conversion of 69%, whereas a dry-gas composition of 2.6%CO, 14.7%CH$_4$, 19.5%CO$_2$, and 63.2%H$_2$ was reported.

US20050025701 patent (Bhat et al. 2005) [70] through in depth investigations led to the invention that certain metal oxides, the metal cations of which are partially and reversibly reducible to lower oxidation states under steam reforming conditions, such as cerium, tin, chromium, molybdenum, tungsten, and vanadium oxides lose their surface oxide ions generating oxygen ion vacancies. The latter serve as active surface centers for H$_2$O dissociation. Over these easily reducible metal oxides, hydroxyl species formation (OH groups) occurs at significantly lower temperatures compared to the conventional supported metal catalysts, and as a result of this the activity of the catalyst increases significantly at these low temperatures. The catalyst compositions reported consisted of (a) Group VIII metal, (b) at least two partially reducible metal oxides chosen from cerium, molybdenum, tungsten, tin and chromium, (c) zirconium oxide, (d) lanthanum oxide, and (e) aluminium oxide. Surprisingly, the inventors found that when two of these reducible oxides are mixed together in the same catalyst composition the resulting catalyst was even more active for the steam reforming reaction. Table 1 lists the catalyst formulations developed and tested.

Some of the results obtained in terms of iso-octane conversion ($X_{\text{iso-Cs}}$, %) and gas product composition in the absence of sulfur in the feedstock are presented in Fig. (5). First, the catalysts Table 1 were tested for the conversion of iso-octane at 923K in the absence of sulfur in the feedstock. Catalysts A-F were also tested in the presence of 20ppm of...
Table 1. Catalytic Formulations Investigated by Bhat et al. [70].

<table>
<thead>
<tr>
<th>Catalyst Code</th>
<th>Composition</th>
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<tbody>
<tr>
<td>A</td>
<td>40%Ni-30%MgO-30%Al₂O₃</td>
</tr>
<tr>
<td>B</td>
<td>15%Ni-30%CeO₂-5%Cr₂O₃-20%ZrO₂-3%La₂O₃-27%Al₂O₃</td>
</tr>
<tr>
<td>C</td>
<td>5%Pt-25%CeO₂-20%V₂O₅-20%ZrO₂-3%La₂O₃-27%Al₂O₃</td>
</tr>
<tr>
<td>D</td>
<td>3%Pd-27%CeO₂-20%Cr₂O₃-20%ZrO₂-3%La₂O₃-27%Al₂O₃</td>
</tr>
<tr>
<td>E</td>
<td>4%Pt-1%Rh-25%MoO₃-20%CeO₂-20%ZrO₂-3%La₂O₃-27%Al₂O₃</td>
</tr>
<tr>
<td>F</td>
<td>5%Pt-25%SnO₂-20%V₂O₅-20%ZrO₂-3%La₂O₃-27%Al₂O₃</td>
</tr>
<tr>
<td>G</td>
<td>4%Pt-1%Rh-25%MoO₃-20%CeO₂-20%ZrO₂-3%La₂O₃-47%Al₂O₃</td>
</tr>
<tr>
<td>H</td>
<td>4%Pt-1%Rh-25%MoO₃-20%CeO₂-50%Al₂O₃</td>
</tr>
<tr>
<td>I</td>
<td>4%Pt-1%Rh-45CeO₂-3%La₂O₃-47%Al₂O₃</td>
</tr>
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</table>

ethyl mercaptan. Catalyst A was deactivated after one day on stream, whereas for the other catalysts an initial decrease in activity was observed. After a few hours on stream, an 80-90% CH₄ conversion was established. It should be mentioned that the distribution of products was not significantly affected; however an increase in the CO/CO₂ product ratio was observed. In particular, the amount of CO in the product stream was found to be higher than that of CO₂, implying that the water-gash shift reaction was affected.

US200702254805 patent (Feaviour et al. 2007) [71] is focused on a supported metal catalyst, where the support mainly contains ceria, iron oxide, chromium oxide, vanadia, and magnesium aluminate. The metal loading was 0.5-10 wt% based on the total weight of support. In an earlier patent, the inventors have disclosed a catalyst comprising of Rh and optionally Pt on a support containing 5-40 wt% ceria, 60-95 wt% alumina and 0-10 wt% alkali metal or alkaline earth metal [72]. The breakthrough of the Feaviour et al. [71] invention was the improved formulation for promoting the reforming reaction over a wide range of temperatures and for different kinds of fuels, including S-containing fuels. The catalysts of this invention were tested in gasoline steam reforming after being diluted with cordierite (cordierite: catalyst, 10:1) and pre-shaped in pellets form. The fuel flow rate was 1.9mL/h, the temperature of testing was 973K, and a S/C ratio of 4 was used. The conversion of the gasoline feed to CO, CO₂ and CH₄ was found to be in the range of 72-94%, while the concentration of non methane hydrocarbons (NMHC) produced was 1-5 vol%; it is noteworthy that lower concentrations of NMHC indicate better catalytic performance. The catalysts of the invention [71] were also tested for dodecane steam reforming. The catalyst containing CeO₂ had a better catalytic performance for reforming S-containing dodecane tested at 1073K.

Kobayashi [65] reported a composite oxide support containing at least one element from rare earths elements (Ce, Y, Zr), and steam reforming catalysts containing at least one of the Ru, Rh, Ir, Pt, Pd, Co, Fe, Au and Ni metals with a mean particle size of 1-15nm. The catalysts invented showed significant activity over gaseous hydrocarbon feedstock, such as methane, ethane, and gasified propane, iso-octane, kerosene and gasoline. The reaction temperature tested was 573-1073K, the S/C ratio was 1.0-6.0, and the GHSV varied in the 150-800,000h⁻¹ range. Examples of the sulphur-containing compounds present in the feedstock material included methyl mercaptan, ethyl mercaptan, isobutyl mercaptan, tert-butyl mercaptan, isopropyl mercaptan, dimethyl sulphide and others. It was found that when the S/C ratio was less than 1.0 decomposition of hydrocarbons resulting to coking occurred, whereas for S/C ratios larger than 6.0 the yield of reaction to CH₄ and H₂ was too low.
US20090108238 patent (Wagner et al. 2009) [73] reported on a catalyst where the main issue addressed was the retaining of high conversion of hydrocarbons into hydrogen with a high stability in catalyst surface area (m²/g). The active metal phase consists of one or more metals selected from the group of Rh, Pd, Os, Ir, Ru, Re and combinations of them. The breakthrough claimed was the support composition, which was a mixture of about 10-60 wt% of low surface area material, and 40 to 90 wt% of a high surface area material. The high surface area material had a BET area of about 80-300m²/g, whereas the low surface area material had a BET area in the 1-10m²/g range. Preferable high surface area materials could be alumina-doped with oxides such as yttria, ceria and zirconia. Another combination of high surface area material is a mixed metal oxide with oxides selected from two or more of the zirconia, ceria, yttria, samaria, molybdenum oxide, manganese oxide and magnesium oxide. Alternatively, high surface area materials were reported to be ceria, silica, titania or mixtures of them. Low surface area materials are of the general formula MeO/alumina, where Me stands for Ca, Mg, Ba, Sr and their combinations. The importance of the invention was that the catalyst with a support consisting of a mixture of low and high surface area metal oxides exhibited a higher CH₄ conversion in the 450-800°C range compared to the catalysts where the support was only a high surface area or low surface area material.

3.1.2. Metal Oxides Thin Film Catalysts

Many catalytic formulations have been developed so far for H₂ production in fuel reforming systems. Different kinds of substrates have been used, such as honeycomb ceramic structures on which a metal oxide (e.g., γ-alumina) and a noble metal (e.g., Pt, Rh, Pd) comprising the catalytic phase are deposited. Metal oxides in the form of powders obtained after grinding were also applied on ceramic substrates. JP10182155 [74] presented methods to obtain metal oxides in the form of powders by preparing oxide precursors from salt solutions of Al, Ce and Zr followed by calcination in air of the yielded oxide precursors. However, with the above-mentioned conventional methods of metal oxide powder preparation, excellent adhesion to substrates (especially to metal substrates) towards formation of thin films is not sufficient giving several limitations to hydrocarbon reforming performances.

US20060172885 patent (Shimazu et al. 2006) [75] reported on a procedure to provide nanoporous metal oxides consisting of ceria, zirconia and alumina with high adhesion on various substrates (e.g., honeycombs), excellent heat tolerance, and improved reforming performance. The composite metal oxide had a ceria content of 10 to 60 wt%, zirconia content of 20 to 90 wt%, and alumina content of less than 70 wt%. Spectroscopic characterization of the catalyst showed that the composite oxide is truly nanocomposite; mixing at the atomic level had been achieved. The nanocomposite oxide in the form of thin films was deposited onto honeycombs and tested for reforming reaction using a S/C ratio of 2.0 and iso-octane as reforming fuel. High conversions of iso-octane of the order of 92% were obtained.

3.1.3. Absorption Enhanced Reforming (AER) of Hydrocarbons

The main aim of Absorption Enhanced Reforming (AER) of hydrocarbons is to combine the chemical absorption of CO₂ gas product with the gasification reactions occurred in a fluidized bed gasifier. The main characteristics of the AER process for efficient and low-cost conversion of fuel into a H₂-rich product gas is the CO₂ removal in the reaction zone of the gasifier, and as a result of this the reaction equilibrium of the water-gas shift reaction (CO+H₂O ↔ CO₂+H₂) is shifted towards further hydrogen production [76]. Removal of CO₂ from the reformate gas if necessary can also be minimized in this AER process. As the CO₂ absorption is highly exothermic, the heat released can be integrated directly into the endothermic gasification/reforming processes. The spent solid absorbent has to be regenerated in a subsequent process step.

Many approaches have been explored towards the development of a fuel reforming technology that uses chemical processes with low energy consumption, and leading to a H₂-rich gas product stream. These include the application of reaction-separation membranes [10] and the application of CO₂ absorption materials. The AER concept seems to be a very promising one when combined with low-cost non-toxic natural materials. In particular, during AER process a methane steam reforming catalyst and a CO₂ natural absorbent (CaO (calcites), or MgO (dolomites), or olivine) can be combined in a single step, so that reforming, water-gas shift and CO₂ absorption chemical reaction steps occur at the same time [76, 77].

Many benefits from the application of the AER process over the conventional CH₄ reforming process have been demonstrated. These include: (a) reforming at significantly lower temperatures (~ 873K) with a simultaneous higher CH₄ conversion, (b) lower cost, (c) H₂ production at gas pressures 200-400 psig and at relatively high purity; (d) minimization of downstream purification steps; (e) elimination of side reactions and increasing catalyst lifetime; (f) lower excess steam used in conventional SMR; and (g) effective remediation of CO₂.

Hampden-Smith et al. [78] reported on materials suitable for performing absorption enhanced reforming of a fuel. Carbon dioxide absorbent materials used were metal oxides from Group 1 and Group 2, whereas catalytic materials for steam reforming and WGS reactions are disclosed. Spray processing was used for the manufacturing of these materials. According to US7578986 patent (Hampden-Smith et al. 2009) [78], the CO₂ absorbent material is composed of CaO:MgO, CaO:Al₂O₃, CaO:TiO₂, CaO:ZrO₂ or CaO:Al₂O₃:MgO. In the above combinations CaO content was at least 30 wt%. The absorbent material is capable of retaining at least 10g of CO₂ per 100g of absorbent where the regeneration step includes treatment of the absorbent at 973K. The reforming catalyst used was a supported metal catalyst. The support comprises metal oxides of aluminium, cerium, zirconium, lanthanum, silicon, zinc and combinations of them. The active metal is chosen among the group of Rh, Ni, Ru, Pt, Pd, and alloys of them. The catalyst was
found to achieve 90% methane conversion at 873K using a S/C ratio of 3:1 and a GHSV of 12,500h\(^{-1}\) in the absence of CO\(_2\) absorbent. In the case of composite material (catalyst and CO\(_2\)-absorbent), the mass ratio of absorbent to the catalyst was in the range of 20:1 to 3:1. Different fuels such as alcohols, gasoline, and diesel were studied. It was found that at 873K the AER process could result in 98% conversion of fuel into H\(_2\) compared to only 75% under normal conditions (absence of CO\(_2\) absorbent). Furthermore, CO concentrations in the 1 vol% range under AER conditions compared to 6-10 vol% CO under normal conditions were reported, whereas the total CO and CO\(_2\) concentration was less than 2 vol% compared to 25 vol% obtained under conventional conditions.

Beyond calcites and dolomites used towards the enhancement of hydrogen production through the AER concept, US20070224111 patent (Essaki et al. 2007) [79] reports on the use of a lithium composite oxide as CO\(_2\) absorbent along with a supported catalyst using an absorbent /catalyst ratio (w/w) of no less than 9. In particular, lithium silicate (Li\(_4\)SiO\(_4\)) is used as CO\(_2\) absorbent according to the following chemical equation:

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3
\]  

(5)

The raw hydrocarbon material used in the feedstock was methane, ethanol or kerosene. The catalyst was a metal supported one, where the metal could be one among the group of nickel, ruthenium, rhodium, platinum, cobalt; the preferable supports used were magnesia, ceria, zirconia and titania. For the sustainability of the process, the regeneration of CO\(_2\) absorbent was also discussed. Temperatures lower than 823K and nitrogen or air (1 bar) were the optimized conditions for absorbent recovery without severe deterioration of its performance. The Reforming reaction was carried out in the 723-843K range. This temperature range is important from a practical point of view since in this range CO\(_2\) absorption is maximized considering the exothermicity of CO\(_2\) absorption process.

For a sustainable AER process, regeneration of the CO\(_2\) absorbent should be taken into account. This issue is discussed by Essaki et al. [80], where a temperature of 898K inside the reactor of CO\(_2\) release and the introduction of an inert gas (e.g., N\(_2\)) were used. When reaction (5) takes place in the forward direction, it was confirmed experimentally that in the case of methane and ethanol reforming it is possible to shift the reaction equilibrium with high-temperature steam, thus promoting hydrogen production, while at the same time the CO concentration is reduced [81]. However, as pointed out in US20080227626 patent (Essaki et al. 2008) [80], the CO\(_2\) absorbent is subjected to a coking problem, particularly when the number of carbon atoms in the feed is increased (ethanol, propane, butane, etc.). The carbon deposits are mainly found on the catalytic surface leading to CO\(_2\)-absorbent degradation.

In the 16\(^{th}\) World Hydrogen Energy Conference a method for CO\(_2\) absorbent regeneration was proposed by Essaki et al. [82], where the release of CO\(_2\) could be achieved at the temperature of 923K within 30 min under nitrogen flow. The carbon deposited on the surface reacted with CO\(_2\) at 898K, making possible the effective removal of carbon deposits according to the Boudouard reaction:

\[
\text{C} + \text{CO}_2(g) \leftrightarrow 2 \text{CO}(g)
\]  

(6)

Due to the equilibrium of this reaction, elimination of carbon is facilitated by increasing the CO\(_2\) concentration in the gas treatment atmosphere. Due to the up-flow of treatment gas (e.g., nitrogen) inside the reactor, the CO\(_2\) concentration in the treatment gas, introduced from the bottom of the reactor, gradually increases as the treatment gas moves towards the top of the reactor. Due to the above considerations CO\(_2\) in the treatment gas is increased.

3.1.4. Steam Reforming of Hydrocarbons for Fuel Cell Applications

Fuel cells can be used in both stationary and mobile systems (e.g., buses, cars and trucks) as alternatives of the various kinds of internal combustion engines used nowadays [10]. The major initiatives for developing fuel cell powered vehicles are the low pollution emissions achieved, high fuel conversion, high acceleration, low levels of noise and vibration, and the potential of using biomass derived alcohols (e.g., bio-ethanol) rather than petroleum-based fuels. For a stand-alone fuel cell power system, the two significant operational requirements are the ability for a quick start-up, and the ability to supply the necessary power and demand for the dynamically fluctuating load. The rapid start-up requirement is obvious. Many different hydrocarbons are considered good candidate fuels for use in transportation applications but most likely alcohols such as methanol or ethanol are favorable fuels for use in fuel cells for transportation applications [10].

US6303098 patent (Kramarz et al. 2001) [83] invention relates to a catalyst for gasoline or diesel steam reforming towards a high hydrogen yield suitable for supplying a fuel cell. The difficulty of converting hydrocarbons (e.g., methane, iso-octane, hexadecane, toluene, etc.), gasoline or diesel into hydrogen is the fact that the hydrogen-oxygen bond is thermodynamically stronger than the carbon-oxygen bond at moderate temperatures. Under thermal equilibrium conditions, the reaction products will be rich in water and poor in hydrogen. In order to produce a hydrogen-rich gas, a bifunctional catalyst is required which can "de-hydrogenate" the hydrocarbon molecule, and then selectively oxidize the carbon-containing fragments formed. CeO\(_2\) was proposed among that family of oxides, including: ZrO\(_2\), Bi\(_2\)O\(_3\), BiVO\(_4\), LaGaO\(_3\) with ionoxic oxygen in their structure for this purpose. Ionic oxygen reacts with the double bonds of a dehydrogenated hydrocarbon fragment towards the formation of C=O entities. The inventors claim that a new class of materials has been developed by combining such oxides with metals which can adsorb hydrogen. These new catalyst formulations can be potentially used towards hydrogen-rich gas formation from a variety of hydrocarbons, such as aliphatic, aromatic, napthenes, olefins and others. In Fig. (6), the product gas composition obtained from the steam reforming of natural gas in the presence of the invented catalyst: 0.5%Pt/C\(_{60.07}\)Sm\(_{0.23}\)CS\(_{0.01}\)La\(_{0.00}\)O\(_{1.85}\) is given. As shown in Fig. (6), under the given conditions 75 vol% H\(_2\) (dry-basis) is produced at temperatures lower than 800K. It should be pointed out that steam reforming of natural gas in
the petrochemical industry is performed at high pressures and at temperatures higher than 1173K. There are many reasons which necessitate the use of lower temperatures for steam reforming such as the wider choice of materials, the higher efficiency, the lower yields of carbon monoxide, the faster start-up process, the latter considered essential in transportation applications.

US20100172826 patent (Kawashima et al. 2010) [84] claims the design of an advanced fuel cell system comprising a reformer employing an excellent reforming catalyst for H2 generation, and a fuel cell employing hydrogen produced by the reformer. The inventors have carried out extensive studies in an effort to attain the aforementioned objective. They found that through the use of a carrier containing MgO and Al2O3 and an additive at least one compound selected from La2O3 and CeO2, surface diffusion of alumina and a-phase nucleation are prevented, thereby maintaining the strength of the carrier even after a long-term thermal history. Ru, Pt, Rh, or Ir component is supported on the carrier in a highly dispersed state, whereby the produced reforming catalyst exhibits high catalytic activity, enhanced heat resistance, and stable activity after long-term thermal history.

Ideally, the reformer should have a rapid start-up and small dynamic response time, and excellent fuel conversion efficiency. The reformer should also have a minimal size and reduced weight as compared to other electric power sources. Reformers operate at temperatures higher than 873K and sometimes higher than 1273K. At lower temperatures, during the start-up period decomposition of carbonaceous fuel onto the catalyst surface could occur, thus affecting the overall performance. The catalytic component is applied on the substrate after using impregnation, washcoating, chemisorption or precipitation techniques [10]. The reformer catalytic substrate should be resistant at high temperatures (up to 1473K) and withstand reducing and oxidizing gas atmospheres, including hydrocarbons, hydrogen, carbon monoxide, oxygen, water, sulphur, etc. Oxygen storage compounds, such as CeO2 or CeO2-ZrO2 solid solutions are considered very beneficial as additive promoters of the catalytic activity. Oxides of yttrium, cerium, lanthanum, prasodymium, neodymium, ytterbium, scandium and combinations of them including oxides of magnesium, calcium, strontium, or barium towards formation of compounds having spinel, magnetoplumbite, hexaluminate, perovskite or fluorite structures have been used for diesel fuel reforming [72]. Desired reaction products for feeding a downstream SOFC includes H2 and CO but unconverted hydrocarbons (CH4, C2H6, C2H4) can be found which could cause problems since a downstream SOFC would only operate very well with minimum hydrocarbons concentration in the reformate gas.

3.2. Steam Reforming of Oxygenated Hydrocarbons (C\text{x}H\text{y}O\text{z})

Oxygenated hydrocarbons are molecules with the general formula C\text{x}H\text{y}O\text{z}. Molecules having a C:O atom ratio of 1:1 include: methanol, ethylene glycol, glycerol, and sorbitol. As shown in Fig. (7) [85], the steam reforming of these oxygenated hydrocarbons towards CO and H2 formation are thermodynamically favourable at lower temperatures than those required for the steam reforming of alkenes with the same number of carbon atoms. For example, the complete reforming of sorbitol yields 13 moles of hydrogen for every 6 moles of CO2 produced according to the following equation:

\[
\text{C}_6\text{H}_{14}\text{O}_6 + 6 \text{H}_2\text{O} \rightarrow 6 \text{CO}_2 + 13 \text{H}_2
\] (7)

Several patents to be discussed next describe methods for the reforming of the aqueous phase of water soluble oxygenated compounds at concentrations of 10 vol% or lower. Thus, there is an imperative need for the development of catalytic systems and processes that have higher activities at higher levels of oxygenated compounds concentrations.

![Product gas composition (vol%) obtained from the steam reforming of natural gas in the presence of the novel catalyst Pt/CSCL: 0.5 wt%Pt/Ce0.75Sm0.234C0.15Li0.001O1.859 as reported by Kramarz et al. [83].](image-url)
Methanol has been used for providing a hydrogen-rich gas stream through steam reforming for mobile combustion engines applications as discussed in US4716859 patent (Konig et al. 1988) [86]. US4988580 patent (Ohsaki et al. 1991) [87] has addressed the issue of supplying the hydrogen-rich gas on demand in a variable demanding environment, but this suggestion is not applicable to small mobile systems.

US5268346 patent (Ino et al. 1993) [88] reports on the development of a catalyst for the steam reforming of light naphtha. The catalyst contains 0.1-2 wt% Ru whereas ceria or rare-earth oxides containing ceria in an amount between 5 and 40 wt% along with 60-95 wt% of alumina are the main components of support. The Ce/Ru atom ratio in the catalyst composition is in the 10-200 range. For the catalytic tests light naphtha with C/H atom ratio of 0.422 and a sulfur content of 0.2ppm was used. The reaction temperature, S/C ratio, and GHSV were kept at 873K, 1.5 and 9,000h⁻¹, respectively. The catalyst having CeO₂ as support (Ce/Ru=58) exhibited 44% naphtha conversion, whereas the carbon accumulated on the catalyst surface was 0.06 wt%. On the other hand, a catalyst with 20 wt% CeO₂-80wt% Al₂O₃ carrier composition, and a Ce/Ru atom ratio of 12 exhibited the highest naphtha conversion (80%). The amount of carbon deposited onto the surface for the best performed catalyst was found to be 0.13 wt%.

Cortright et al. [89] described a method for H₂ production via steam reforming of a different category of oxygenated hydrocarbons, such as glycerol, glucose and sorbitol. This method was proved to be beneficial at lower reaction temperatures than the conventional steam reforming of alkanes. In a following improved patent (US6964757) [89], the same inventors claim a method for H₂ production through steam reforming of methanol, glycerol and sugars (e.g., glucose, xylose). The method takes place in the liquid phase and at lower temperatures than the conventional steam reforming of alkanes.

US20070258882 patent (Castellano et al. 2007) [90] reported on the development of a catalyst for alcohol steam reforming which exhibits both high activity for methanol steam reforming and good CO₂ selectivity. The catalyst comprises of Pd, yttrium and cerium oxides. A desirable amount of yttrium and optionally Zn may be added. For fuel cell applications, CO present in the reformate product gas stream is poisonous for the Pt electrodes, therefore, any significant reduction in the CO concentration level with the least cost would appear as a significant advance towards the design of efficient steam reforming catalysts. In addition, in the state-of-the-art catalysts for methanol steam reforming, it is difficult to have good alcohol activity and CO₂ selectivity at the same time. Often an increase in one of these parameters results in a decrease of the other. Yttrium is added for withstanding exposure at high temperatures for steam reforming, whereas Zn contributes to a high CO₂ selectivity. At 478K the invented catalysts showed at least 10% methanol conversion and at least 90% CO₂ selectivity.

An improved catalytic system for steam reforming of oxygenated compounds is reported in US20090211942 patent (Cortright et al. 2009) [85]. The active phase used comprises of Re, Pd, Ni, Ir, where monometallic and bimetallic catalysts from this group of metals were tested. In the case of bimetallic catalysts, Re was preferably the second metal, and M:Re atom ratios were in the 1:1-1:16 range (1:16 in the case of Ni as primary metal). Rhenium addition was found to enhance the steam reforming activity of higher feed concentrations of ethylene glycol. Carbon was used as support after different treatments, such as oxidation, functionalization through chemical treatment with hydrogen peroxide, and doping with vanadium and titanium. The V and Ti dopants greatly enhanced the sorbitol steam reforming activity. The activity of Rh/Re and Pt/Re bimetallic catalysts was also boosted with Ce and La addition which promoted H₂-selectivity versus CO₂- and alkanes-selectivity. All these catalyst formulations were tested for ethylene glycol steam reforming in the 373-723K range.

A very recent US7659227 patent [91] (Wolf 2010) describes a catalyst for the production of hydrogen from methanol steam reforming mainly composed of Cu/Zn and promoted by the use of Zr or Ce, whereas some Pd or another noble metal can be added. Some of these catalysts contain a Cu/Zn ratio of 5/5 to 8/2 with 0.1 and 2 wt% Pd. Other compositions contain either Ce or Zr (Cu/M equal to 7/1 and 7/2) and 1 wt%Pd. The inventors showed that the Ce or Zr addition, especially in the presence of Pd, had a positive effect on catalytic activity. In the case where both Ce and Zr were added, the activity was found to be less than in the case of addition of the single components. It is important also to mention that at low methanol conversions (< 20%) there was almost no hydrogen production since the main reaction was that of combustion. In the conversion range of 30-80%, a linear relationship was noticed in terms of hydrogen production and conversion since under these conditions other reactions became significant, such as methanol decomposition and water-gas shift. In the high
conversion range (80-100%) the reverse water-gas shift was the dominating reaction.

### 3.3. Auto-thermal Reforming (ATR) of Oxygenated Hydrocarbons

Auto-thermal reforming (ATR) is a combination of both steam reforming (endothermic) and partial oxidation (exothermic) reactions. ATR has the advantages of not requiring external heat and being simpler and less expensive than steam reforming of methane (SRM) [2, 10, 92]. The range of operation of a fuel processor for hydrogen production is depicted in Fig. (8) [92]. The selection of operation conditions of the reformer depends on the specific target. A main target is the high hydrogen yield with low carbon monoxide content. Maximum hydrogen efficiency and low carbon monoxide content is possible for a steam reforming operation. However, steam reforming is an endothermic process and therefore energy demanding. This energy has to be transferred into the system from the outside. In case of mobile reformer units, start-up-time and start-up-energy-demand should be also as low as possible. Therefore, the partial oxidation or auto-thermal operation is preferred [10, 92].

Some of the most popular members of oxygenate hydrocarbon molecules are methanol and ethanol, the steam reforming of which can be expressed by the following endothermic reactions [93-96]:

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3\text{H}_2 & (8) \\
\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} & \rightarrow 2\text{CO}_2 + 6\text{H}_2 & (9)
\end{align*}
\]

Among the liquid fuel sources, C₂H₅OH is a good candidate for several reasons: (i) it is renewable and is becoming increasingly available, (ii) it is easy to transport, biodegradable, and of low toxicity, (iii) it could be easily reformed in the presence of water to generate a hydrogen-rich gas mixture, and (iv) it can be produced free from catalyst poisons such as sulfur [96].

The Cu/Zn-based catalyst disclosed in JP05261288 patent (Tsukuda et al. 1993) [97] shows high reaction selectivity towards H₂ in the methanol steam reforming. However, this catalyst requires a reduction process to be performed in the 523-573K range prior to use. To overcome this problem, Haga et al. [98] report on the development of a triple layered structured catalyst which addresses the above problem. The compositions of the layers are presented in Table 2. It is known that under auto-thermal reforming (ATR) conditions [10] the traditional Cu-Zn catalysts degrade, whereas in the case of a noble metal-based catalyst, which exhibits excellent durability, an increased CO concentration is achieved. These catalytic formulations have been claimed to provide an ATR process with small CO concentrations and a high catalytic performance. According to this invention [98], the catalytic component in the 2nd layer accelerates the combustion reaction, while component IIB accelerates the steam reforming reaction; the catalyst can be heated in a shorter time. It was found that the catalyst with Pd-Zn-CeO₂-ZrO₂ as catalytic components in the 2nd layer presented excellent durability.

CeO₂-based catalysts have been reported to be efficient for a self-sustaining reforming process, where combination of the oxygen and steam presence in the feed was used. Different hydrocarbons were used as fuel, such as methane, iso-octane, gasoline and aviation fuel [99]. In the case of self-sustaining heptane and gasoline reforming, H₂ concentrations of 22 and 28.5 vol%, respectively, were obtained. When n-octane was used as fuel, all n-octane was converted to a reformate mixture of 37 vol%H₂, 12 vol%CO₂, 7 vol%CO and N₂. In the case of iso-octane, the reformate gas composition was found to be 33 vol%H₂, 15 vol%CO₂, 5 vol%CO and N₂. In both cases no deactivation was observed after 4 h on stream. When an aviation fuel was used, at 873K the dried reformate contained 28 vol%H₂, 14 vol%CO₂, 3 vol%CO and N₂, while after one hour on stream some catalyst deactivation was noticed.

Critical issues are still open in the literature regarding auto-thermal reforming as addressed in US20040204315 patent (Krumpelt et al. 2004) [100], where a catalyst for ATR-hydrocarbon fuel cell applications was reported. In particular, the breakthrough of the invention was that it brings a technical solution in the fuel processing through a design of a cost-efficient and stable catalyst. According to the inventors, state-of-the-art catalysts which contain Rh supported on a refractory oxide results in a significant cost to
LaAl0.95Ru0.05O3, La0.8Sr0.2Cr0.95Rh0.05O3 and La0.9Ce0.1Cr0.95

catalyst changes. Among the compositions investigated were

higher temperatures leads to coke minimization but at the

activity deterioration. However, operating the reformer at

Fig. ( into H2-rich reformate (mixture of mainly H2, CO, CO2 and

compounds contained in the diesel fuel are hardly reformed

temperature of operation is required since aromatic

transition metals, and stabilizing elements for sustaining

oxide containing rare-earth elements, catalytically active

catalysts developed in this invention exhibit good activity

and/or lanthanide elements (CexM1-xO2, where M=Zr, Y, La,

2010) involves the use of cerium oxide- based catalysts with

steam/carbon (S/C) ratios in the 1.0-3.0 range [100].

second class of WGS reaction catalysts is based on copper

First in the HTS and then to the LTS water-gas shift reactor,

third class of catalysts includes sulfur-tolerant materials which have as

active phase cobalt and molybdenum sulfides. Mo is usually

dispersed onto a metal oxide support, such as Al2O3, MgO,

ZnO, Mg-aluminate, Zn-aluminate, etc. [8]. Due to the fact that these catalysts can potentially be used in sulfur

containing sour-gas streams, they are called sour gas-shift catalysts. Besides the above mentioned types of catalysts, a fourth class of catalysts relates to metal-containing catalysts. Iron-based catalysts are less active at lower temperatures, and for this reason in order to achieve higher CO conversions in the 463-523K range, a catalyst based on Cu-ZnO was developed in the early 1960s, which is largely used by the industry [102]. Nowadays, the industrial WGS process takes place in a series of two adiabatic reactors, where the stream from the reformer reactor system is passed first in the HTS and then to the LTS water-gas shift reactor, the latter operating at a significantly lower temperature in order to shift the equilibrium (Rxn. 3) toward the desirable hydrogen product with maximum CO conversion.

### 4.2. Low-Temperature WGS Reaction Catalysts

As previously mentioned, current industrial low-temperature (423-573K) WGS is operated using CuO/ZnO-based or CuO/Cr2O3-based catalysts. When a Cu-based low-temperature CO shift catalyst is used a high activity is obtained. However, such a Cu-based catalyst should be subjected to reduction for activation prior to any use. Furthermore, in order to avoid overheating of the catalyst, as a result of the heat generated during activation, it is necessary that the catalyst be processed for a long period of time with a reducing gas. Since the activated catalyst can be re-oxidized and deteriorated when mixed with oxygen, some anti-oxidation treatment is needed. However, Cu-based catalysts have large heat capacity and cannot be rapidly heated during the start-up of reactor, thus gradual heating is needed. On the other hand, when an Fe-based catalyst (HTS) is used, the catalyst is easily heated during start-up period since the catalyst has a low heat capacity and can be heated up to 773K with no strict precautions. These shortcomings can be avoided by appropriate modification of catalyst composition.
US4906448 patent (Sauvion et al. 1990) [103] claims the development of catalyst using Mo and/or Co, and optionally alkali metals deposited on alumina support. This catalyst was reported to exhibit excellent results in CO conversion and H₂ selectivity in comparison with other catalytic systems tested in the 473-623K range and at pressures in the 5-140 bar range. The Ni(Co)/Mo(Ni)/CeO₂ catalyst was found to be stable in the presence of up to 4 vol% S-containing compounds in the feed, such as H₂S, COS, CS₂ and CH₃S. It is noteworthy that a prior art catalyst with composition Co/Mo/Al₂O₃ presents at 548K CO₂ and CₙH₂ₙ₊₂ selectivities of 99% and 1%, respectively, and a CO conversion of 55%. On the other hand, the particular Co/Mo/CeO₂ catalyst exhibited CO₂ selectivities of 100% and a CO conversion of 67.6%. The US4906448 patent (Sauvion et al. 1991) [103] is a following work which claims an improved Ni/Mo/CeO₂ catalyst in terms of CO conversion (69.1% at 548K) and stability with time on stream.

WO0048261 patent (Harada et al. 2000) [104] describes the use of Pt supported on titania in which rare-earth elements have been incorporated (La, Ce). These catalytic systems usually contain as additives alkali or rare-earth elements not deposited in the pore system of titania. Thus, only the noble metal supported on the outer part of the carrier, where the additive is also present can perform. Inventors stated that Pt supported on ceria is prone to deactivation because ceria interacts with CO₂ and H₂O towards carbonate and hydroxide formation which in turn could decorate the Pt metal surface. This is a good reason for using CeO₂-ZrO₂ solid solutions, exploiting, therefore, the imposing thermal stability property of zirconia phase. However, in some cases pure CeO₂ phase remains due to phase separation out of the CeO₂-ZrO₂ composite oxide. Therefore, a desirable catalyst for CO removal and use in fuel cell electricity generation applications should overcome the above mentioned problems. Tagushi et al. [105] describe the effect of Zr addition in ceria on WGS activity. When Zr loading becomes less than 0.5 wt% the catalytic reaction rate increases. On the other hand, when Zr loading is larger than 5 wt% the catalytic activity drops, while the minimum CO concentration is slightly increased and the non desirable methanation rate (CO/H₂ → CH₄) increases. The invention of Tagushi et al. [105] involves a Pt-based catalyst with excellent heat capacity as well as oxidation resistance and a higher low-temperature activity than Fe-Cr-based catalysts. A number of similar catalytic systems have been disclosed. For example, JP20000302410 patent (Taguchi et al. 2000) [106] discloses a cerium-zirconium composite oxide used as carrier of a noble metal. A similar noble metal catalyst having Pt, and optionally Re and Pt supported on zirconia carrier is disclosed also in JP20013215680 patent (Mizobuchi et al. 2001) [107].

Ruettinger et al. [108, 109] invented a supported-Pt catalyst using CuO/CeO₂/Al₂O₃ as carrier, where CeO₂ is a promoter characterized by low pyrophoricity, high mechanical strength, and high heat capacity. Also, the oxide support can be alumina, silica, zirconia, titania, zeolite or a combination of them along with a reducible metal oxide among molybdenum, vanadium, cerium, neodymium, praseodymium, titanium, manganese and nickel. Preferably, alumina and ceria are used as a support and reducible oxide, respectively. Two loadings of Pt were tested (0.02 and 0.1 wt%) using a feed stream consisting of 7.4 vol% CO, 32.3 vol% H₂O, 31.82 vol% H₂ and N₂ as balance gas at a flow rate of 1.5L/min. The catalysts were found to exhibit no significant deactivation and particularly in steam exposure at low temperatures (c.a. 493K). This is a serious problem encountered in the WGS reaction process using non pyrophoric copper-based catalysts as disclosed in the US6913739 patent (Shore et al. 2005) [110]. The latter is extremely important during start-up and shutdown operations of the WGS reactors containing Cu-based catalysts, where the temperature decreases below the dew point of the water content present in the feed gas stream. The pyrophoricity of the invented catalysts was measured using Differential Scanning Calorimetry (DSC). The industrial Cu-Zn catalyst (UCI) exhibited the highest exothermicity, whereas the 8%CuO/15%CeO₂/Al₂O₃ catalyst the lowest one. Also, the Pt/CeO₂/Al₂O₃ catalyst showed comparable or higher catalytic activity than the pyrophoric Pt/CeO₂ catalyst. Comparable levels of WGS activity for low-pyrophoricity CuO/CeO₂/Al₂O₃ and pyrophoric WGS catalysts were also

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Fig. (9). Reforming efficiency (%) with steam/carbon (S/C) ratios in the 1.0-3.0 range for different catalytic systems [100].

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Ceria-based Catalytic Materials for Hydrogen Production Via Hydrocarbons Recent Patents on Materials Science 2011, Vol. 4 No. 2
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found. The same inventors [111] reported also on an improved Pt-based catalyst for WGS reaction with a very low methane production rate. The catalyst is composed of 0.1 wt% Pt, an anti-methanation agent such as SnO₂ in an amount of 0-7 wt%, GaO₂ or mixtures of them, and the support was one among alumina, titania, rare-earth oxides or mixtures of them. The catalysts were evaluated in terms of CO conversion and methane production using a reactant gas consisting of 3%CO/15%CO₂/48%H₂/34%N₂/26%H₂O. The improved 2%Pt/7%SnO₂/CeO₂ catalyst exhibited at 519K a CO conversion of 50% and 1.5ppm of CH₄ in the product gas stream, whereas the 2%Pt/CeO₂ catalyst showed a CH₄ formation of 100ppm, and 50% CO conversion at 494K.

For further optimization of the operating conditions towards reducing the aging effects, Ruettinger et al. [112] invented a bimetallic Pt-Re catalyst for generating hydrogen by the WGS reaction. The Pt-Re catalyst used is supported on an inorganic oxide carrier with a high surface area, including alumina, zirconia, titania, silica, and rare-earth metal oxides and mixed oxides of the above mentioned oxides (e.g., ceria-zirconia). It was found that the stability and prolonged effective operation of supported Pt-Re catalyst depends on various parameters, such as CO content (5-15 vol%) in the feed, temperature (513-633K), gas hourly space velocity (GHSV, 5,000-45,000h⁻¹) and Pt loading (wt%). It was found that the activity of these catalysts is maintained under these conditions but drops at conditions outside of this range. For a given Pt loading it was found that low space velocity, high temperature, and low CO content are appropriate catalyst’s running conditions.

Wagner et al. [113] investigated the effect of metal promoter on WGS catalysts and reported on the development of a catalyst based on Group VIII and Group IB metals, a transition metal promoter selected from the group consisting of Ru, Nb, Ag, Mn, V, Mo, Ti, W or a combination of them, and a ceria-based support. Figure 10 presents the dependence of CO conversion on reaction temperature for a series of catalysts developed. Research studies [114] have shown that for transition metals in the zero oxidation state which are used in the WGS reaction, the catalytic activity follows the order: Cu>Re>Ru>Ni>Pt>Os>Fe>Pd>Rh Ir. The key criterion for metal selection is the technical application and the gas atmosphere encountered by the catalyst (CO, H₂O, H₂ and CO₂ feed concentrations). Therefore, not only the relative activity of the metal does matter but also its selectivity and its capability to retain its activity after exposure to condensing or oxidizing gas atmospheres. It should be taken into account that in fuel cell applications the catalyst volume is usually extremely small (0.01 to 0.1m³), and therefore research should seek for metals of high activity. Different CeO₂-based mixed metal oxides were tested in this disclosure [113]. Since the WGS reaction activity is affected by the addition of a second oxide into the CeO₂ matrix or on its surface, additives such as Gd, Sm, Zr, Li, Cs, La, Pr, Mn, Ti, W were used in the concentration range of 0-90 wt% towards enhancement of CeO₂ activity. Catalysts containing Pt as active phase and Re as promoter with a Pt:Re atom ratio of 3:1 exhibited a CO conversion of 90% at 498K.

Thompson et al. [115] claim that the issue of insufficient durability and activity presented by the conventional WGS catalysts could be faced by the use of a Au/CeO₂-based catalyst. The main contribution of this patent was the preparation of a reducible oxide support containing cerium oxide, cobalt oxide, zinc oxide, iron oxide or combinations of them. The support was prepared using two different approaches, namely, precipitation and temperature programmed reaction of cerium acetate or cerium carbonate with air in order to assess the effect of synthesis method on the WGS activity. WGS reaction was tested at 513K and it was found that 5wt%Au/CeO₂ catalyst exhibited superior performance compared to a commercial Cu-Zn-Al catalyst. In particular, the reaction rate was varied in the 5-293μmol/g range over supported Au catalysts, depending on the temperature programmed reaction conditions applied to be compared to 59.5μmol/g obtained over the Cu-Zn-Al catalyst. Another supported Au catalyst containing Re in the 5:1-1:5 (w/w) ratio was disclosed in the US20030012719 patent (Roos

Fig. (10). CO conversion as a function of temperature in WGS over Ce-Zr-O based catalysts [113].
et al. 2003) [116]. The support was based on alumina, titania, ceria, zirconia, lanthana and mixtures of them. This patent bridged the existing gap in the patent literature between the well known high activity Au catalysts and the practical use of these catalysts for CO removal from real reformate gas streams.

According to the Department of Energy (DOE) of the USA, when conventional HTS and LTS catalysts are used, the WGS reactor takes one third in volume of the fuel reformer. Thus, minimization of space requirements by the development of highly active catalysts is a key challenge, especially when the final application is for fuel cells operation. The activity of conventional Cu/ZnO/Al2O3 catalysts varies according to the gas-atmosphere (reducing versus oxidizing). At 523K, the catalyst is prone to sintering and exhibits poor S-tolerance [117]. US20050238574 patent (Moon et al. 2005) [118] discloses a catalyst with composition of 0.4wt%Pt-3wt%Cu-62wt%Ni/CeO2 which exhibits a much better WGS activity in comparison with conventional LTS catalysts, namely, Cu-Zn/Al2O3, Pt/CeO2, Ni/CeO2 and Pt-Ni/Al2O3. The latter catalyst appears as potential catalyst for LT-WGS, especially due to its good thermal cycling stability and considering the low amount of Pt used; only 0.4 wt% of Pt was used compared to 4.0 wt% Pt used in conventional catalysts. A catalyst with composition 0.4wt%Pt-3wt%Cu-62wt%Ni/CeO2 presented 54% and 90.7% CO conversion at 493 and 573K, respectively, and retains its activity after 120h on reaction stream (~70% CO conversion).

A new class of catalytic support materials for metals to be used in WGS reaction with the general formula (Na_{0.33}A_{0.66})_2B_2O_7 (pyrochlore-type oxides) has been proposed in US20070269359 patent (Fisher et al. 2007) [119]. In the above formula, A is one of the lanthanide metals, B is one or more metals chosen from the group of Ti, Sn, Ge, Ru, Mn, Ir, Os and Pb, and δ is a number in the 0-1 range. Compounds such as (Na_{0.33}Ce_{0.66})_2Ti_2O_7, (Na_{0.33}Ce_{0.66})_2Ti_2SnO_7, (Na_{0.33}Ce_{0.66})_2Ti_2Ge_2O_7 and (Na_{0.33}Ce_{0.66})_2Pt_2O_7 belong to the series of supports developed. Supported-Au catalysts were then prepared using the aforementioned supports and compared with Au/CeO2 and Au/Ce-Zr-O catalysts (reference catalyst). The pyrochlore-type oxides presented a comparable activity with the supported-Au reference catalyst, where the former catalyst was claimed to be stable and very active, particularly at low temperatures.

In the US20070179053 patent (Lee et al. 2007) [120] the inventors focused on the preparation of active supported-Pt catalysts having as support a composite oxide of CeO2-Al2O3 or CeO2-ZrO2 towards the low-temperature WGS reaction. The incipient wetness impregnation and sol-gel techniques were used for the deposition of Pt and the production of support, respectively. The invented catalysts presented over 90% CO conversion values.

A process for improving the activity of Au/CeO2 and Pt/CeO2 catalysts by adding 0.1-2.0 vol% oxygen in the WGS reaction feed stream was reported in US20080260607 patent (Flytzani-Stephanopoulos et al. 2008) [121]. The inventors claimed that after removing the Pt or Au nanoparticles by cyanide leaching, the catalyst became active with just a tiny amount of metal (e.g., for Au one tenth of the nominal amount used) due to the unraveling of Pt_{n-O-Ce} clusters formation. They showed that metal nanoparticles of Au or Pt [121] are not important for the LT-WGS reaction for catalytic systems where CeO2 is used as support, since only Au_{n-O-Ce} or Pt_{n-O-Ce} moieties are the active sites for the WGS reaction. A tiny amount of the metal in the oxidized state is needed in the active phase, which is a very cost-effective way for active supported noble metal catalysts. This invention describes methods of making active stabilized Au/CeO2 catalysts for LT-WGS. In Fig. (11) the effect of oxygen addition in the feed is presented for the catalyst made and operated according to this invention. As previously

![Fig. (11). The effect of added oxygen in the WGS reaction over catalysts made and operated according to the patent invention US20080260607 [121].](image-url)
mentioned, an important aspect of this invention was the discovery that Au metal particles are a kind of “spectator species” for the water-gas shift reaction.

Recently, Ilinich et al. [122] reported a water-gas shift catalyst comprising platinum group metals (Pt, Pd, Rh, Ru, Ir) dispersed on an inorganic oxide support (e.g., Al₂O₃) modified with a carbon-containing burn-out additive, and a rare earth oxide (e.g., La₂O₃, CeO₂, Pr₆O₁₉, Nd₂O₁₉, Eu₂O₃, Sm₂O₃, Gd₂O₃). Examples of burn-out additives include sugars, starches, and lignin or grain flours such as wood, wheat, corn, rye, etc. Water soluble polymers such as polyethylene oxide or polyvinyl alcohol can also be used. The inventors reported that the initial activity of the catalysts comprising an inorganic oxide support, a platinum group metal, and a rare earth component, can be enhanced by the addition of alkali metal compounds. In particular, it has been found that the addition of compounds of lithium, sodium, potassium, rubidium, and cerium increases the initial catalytic activity. Figure 12 shows the initial WGS activity of Na-promoted catalyst (Example 10) vs. a catalyst without Na (Example 8). As clearly illustrated, in the whole temperature range investigated the Na-promoted catalyst yielded significantly lower CO concentrations at the reactor outlet compared to the non-promoted analog. The process application of the invention is particularly effective when CO feed concentrations do not exceed the value of 20 vol%.

Table 3 provides a summary of important recent patented supported metal catalyst compositions related to the use of ceria as support or additive for the Low-Temperature Water-Gas Shift reaction.

### 4.3. High-Temperature WGS Reaction Catalysts

One of the concerns of HT-WGS catalysts (T>573K) is the formation of CH₄ which is the result of the following reaction steps:

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

The above reactions are favourable with noble metal-based catalysts, and as a consequence of that lower hydrogen yields are obtained. Korotkitk et al. [123] proposed a low-cost catalyst suppressing methanation reaction, namely Pt/CeO₂-ZnO. When a reference 0.5 wt%Pt/Al₂O₃ catalyst was tested in the 373-682K range, the latter catalyst resulted in the production of significant amounts of CH₄ at 682 K, whereas in the case of invented catalyst no methane production was noticed. The inventors stated that a basic metal oxide, such as MgO, CaO, SrO, BaO or ZnO reduces CH₄ formation, whereas CeO₂ was among the most effective promoters used.

Suppression of methanation was also reported in US7238333 and US20050005520 patents (Faur-Ghenciu et al.) [124, 125] but this occurred at lower reaction temperatures (473-698K). The WGS reaction catalysts developed with high activity consisted of a noble metal, among Pt, Pd, Ru, Ir, or mixture of them with a total of 1.0-4.0 wt% metal loading, supported on a ceria-zirconia or ceria-lanthana solid carrier, where CeO₂, ZrO₂ and La₂O₃ loading was in the 20-92 wt%, 20-42 wt% and 8-80 wt% range, respectively. Anti-methanation agents (copper or manganese or iron compounds) were used as additives, whereas promoters, such as yttrium, cesium, lithium, potassium, magnesium, strontium, barium, calcium, or combinations of them were also added. Dopants in the support were also used such as Pr, Nd, La, or combinations of the latter. In some cases, no methane formation was measured for temperatures up to 873K. The catalysts having ceria-zirconia as support performed better under the WGS reaction conditions in comparison with ceria-lanthana supports. Possible explanations for this performance could be the enhancement of: (i) water adsorption, (ii) metal dispersion, and (ii) thermal stability as compared to the case of Ce-La-O, CeO₂ or ZrO₂ used as supports. Pt supported on Ce-Zr-O was found to be the most efficient combination of metal/support compared to Pd, mixtures of Pt and Pd, or mixtures of Pt and Ir. The presence of alkali and alkaline earth metal promoters was found to reduce methanation activity. It is important to notice that CH₄ formation was limited in the 623-648K range. Moreover, it

Fig. (12). Graph comparing the initial activities of Na-promoted and non-promoted catalysts during water-gas shift reaction [122].
was found that CuO shift the methanation reaction at T> 873K, whereas iron was found to be more efficient anti-methanation agent than manganese.

Wagner et al. [126] disclosed a HT-WGS catalyst (723-1173K) comprising Re supported on high surface area supports (ceria-zirconia mixed metal oxide with some additives) in order to substitute Pt, Rh, and Ru noble metals, which promote the methanation reaction. The breakthrough of this invention was that by substituting precious metals and using Re metal the methane production and the levels of higher hydrocarbons were both significantly reduced.

A large number of patents appeared which report the use of CeO$_2$-based catalysts towards the WGS reaction at high temperatures, pressures, and sulphur levels, where Pt metal is the most preferable, and Re is used as additive or promoter [126-132]. For example, US20070264174 patent (Willigan et al. 2007) [127] reports on HTS catalysts where the support contains Ce-based binary, ternary or quaternary mixed metal oxides having an average primary crystal size of 4 nm (after calcination at 773K) and a surface area of 150 m$^2$/g. The mixed metal oxides comprising mainly Ce, Zr or Hf and Ti exhibit a fractal morphology which provides the necessary conditions for fast gas diffusion (low internal mass transfer resistance) and reaction, thus minimizing the need for the design of a catalyst with large pore structure. Pt metal is preferable (0.1-6.0 wt%), whereas Re is used as an additive.

The catalytic support presented in this invention is an improved material of that previously reported in US20060233691 patent (Vanderspurt et al. 2006) [128]. The material disclosed exhibited high activity at high temperatures and high feed CO concentrations, though its performance was limited to high operating pressures and high sulphur levels. In the case, where a membrane-type reactor would be the preferable choice for the WGS reaction, high operational pressure is a key parameter to be tested. Vanderspurt et al. [128] proved with atomistic model that a mixed metal oxide of Ce/Zr/Hf/Ti exhibit a beneficial composition for the WGS reaction at elevated temperatures, pressures and sulphur levels. It was predicted that the inclusion of Ti with Ce and Zr or Hf would lead to lower S and CO binding energies than the equivalent composition without Ti. Comparative results are presented for Pt/Re-Ce$_{0.52}$Zr$_{0.38}$W$_{0.10}$O$_2$ [128] and Pt/Re-Ce$_{0.33}$Zr$_{0.33}$Ti$_{0.33}$O$_2$ [127] catalytic systems, where a superior performance for the latter catalytic system was found.

A similar Pt-based catalyst having Re as a promoter of catalytic activity was reported in the US20070249496 patent (Wagner et al. 2007) [129]. In this invention other promoters such as Nb, Ag, Mn, V, Mo, Ti, W or a combination of them, were also added. It was found that when the metal concentration (Pt+Re) is kept constant at about 4 wt%, the higher the Pt concentration the higher the conversion of CO

### Table 3. Brief Description of Important Recent Patents Related with Ceria-based Catalysts for the LT-WGS Reaction.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Support</th>
<th>Additives/ Promoters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo, V, W, Co, Ni</td>
<td>CeO$_2$, ZrO$_2$</td>
<td></td>
<td>[103]</td>
</tr>
<tr>
<td>Pt, Pd</td>
<td>TiO$_2$, Fe$_2$O$_3$, ZnO</td>
<td>La$_2$O$_3$, CeO$_2$</td>
<td>[104]</td>
</tr>
<tr>
<td>Pt, Re</td>
<td>CeO$_2$, ZrO$_2$</td>
<td></td>
<td>[105, 106]</td>
</tr>
<tr>
<td>Pt, Pd, Rh, Os, Ir, Ru</td>
<td>CuO (Cr$_2$O$_3$, V$_2$O$_5$, MoO$_3$, CeO$_2$, Nd$_2$O$_3$, TiO$_2$, NiO, MgO, Co$_3$O$_4$)</td>
<td>SnO$_2$, Ga$_2$O$_3$</td>
<td>[108, 111]</td>
</tr>
<tr>
<td>Pt, Re</td>
<td>Al$_2$O$_3$, TiO$_2$, ZrO$_2$, SiO$_2$</td>
<td>(La$_2$O$_3$, CeO$_2$, Eu$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$, In$_2$O$_3$, Nd$_2$O$_3$, Pm$_2$O$_3$)</td>
<td>Mo$_3$O</td>
</tr>
<tr>
<td>Au</td>
<td>CeO$_2$, Co$_2$O$_3$, ZnO$_2$, Fe$_2$O$_3$</td>
<td></td>
<td>[115]</td>
</tr>
<tr>
<td>Au, Re</td>
<td>Al$_2$O$_3$, TiO$_2$, CeO$_2$, ZrO$_2$, La$_2$O$_3$,</td>
<td></td>
<td>[116]</td>
</tr>
<tr>
<td>Cu, Ni, Pt</td>
<td>CeO$_2$</td>
<td></td>
<td>[118]</td>
</tr>
<tr>
<td>Au, Ag, Pd, Rh, Ir, Ru, Os</td>
<td>(Na$<em>{0.18}$A$</em>{0.6}$V$_{0.6}$)$_2$B$_2$O$_7$</td>
<td>Na</td>
<td>[119]</td>
</tr>
<tr>
<td>Pt</td>
<td>(Zr$_2$O$_7$, Al$_2$O$_3$, TiO$_2$)</td>
<td></td>
<td>[120]</td>
</tr>
<tr>
<td>Au, Pt</td>
<td>CeO$_2$, La$_2$O$_3$, (Al$_2$O$_3$, TiO$_2$, ZrO$_2$, MgO, Fe$_2$O$_3$, ZnO)</td>
<td>Li, Na, K, Rh, Ce</td>
<td>[121]</td>
</tr>
<tr>
<td>Pt</td>
<td>Al$_2$O$_3$, CeO$_2$, Pm$_2$O$_3$, Nd$_2$O$_3$, Eu$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$</td>
<td>carbon-containing</td>
<td>[122]</td>
</tr>
</tbody>
</table>
obtained. The Pt:Re ratio was varied from 1:1 to 9:1, where a catalyst with Pt:Re ratio of 3:1 exhibited the best performance. When instead of CeO₂ other mixed metal oxides of Ce-Gd-O, Ce-Mn-O and Ce-Sm-O were used, it was found that Ce-Zr-O was the most promising support for Pt/Re-containing catalysts. Surprisingly, from all the compositions studied those rich in Zr, for example Ce₀.₂₅Zr₀.₇₅O₂ were found to be the most efficient in terms of CO conversion and reduction in methanation activity. In another patent from the same group [130], supported metal catalysts having a ceria-based support were claimed. In the support other additives could be introduced, such as Gd, Li, Cs, La, and Nd. The importance of the latter patent was the use of clean precursor materials for the support synthesis, since sulphur, chlorine, sodium, and iodine are known poisons of the WGS activity. For example, in the case of supported Pt catalysts, platinum tetra-amine hydroxide, platinum tetra-amine nitrate, platinum oxalate, and platinum nitrate were used. In the case of platinum tetra-amine hydroxide precursor the ultimate catalyst exhibited greater CO conversions than the catalysts prepared using the other Pt precursors [130].

A bimetallic Pt-Re catalyst supported on an inorganic oxide, such as alumina, zirconia, silica, or ceria-zirconia chemically promoted by an inorganic oxide (e.g. MoO₃) was presented in the US7357911 patent (Ruettinger et al. 2008) [132]. Patent invention claimed a variety of operational conditions which reduce the aging process and provide a stable operation. For that reason, reaction temperature, CO feed composition, S/C ratio and GHSV (h⁻¹) were varied in the 513-633K, 5-15 vol%, 1:1 to 20:1, and 5,000-45,000h⁻¹ range, respectively. WGS activity was tested in the 473-673K range, whereas the addition of small amounts of hydrocarbons and olefins in the feed stream was also investigated. According to the inventors and what reported in the literature [133], there are two competitive processes which adjust the stability of the catalyst against Pt sintering and its subsequent catalytic activity loss. One process is the formation of Pt-carbonyl compounds which weaken Pt-support interactions and increases Pt mobility on the surface, leading, thus to Pt sintering. The other process is the removal of adsorbed CO from the Pt surface. This process provides a cleaning pathway of the surface. A balance between these two processes determines whether catalyst activity with time on stream remains stable. It was found that the higher the CO flow rate the higher the rate of formation of Pt-carbonyl compounds and Pt sintering. As temperature increases the amount of adsorbed CO on the Pt surface decreases, and likely a mobile Pt species is formed. Also, at higher temperatures the cleaning mechanism and desorption of CO becomes faster.

A most recent US20090118119 patent (Ratnasamy et al. 2009) [131] discloses another Pt-Re supported catalyst on a blend of low-surface area (hexa-aluminate) and high-surface area (ceria/zirconia with some additives) supports. The contribution of this invention is the high activity and selectivity of the catalysts at high pressures (ca. 3.4 bar) and temperatures. As inventors stated, when conventional WGS catalysts are modified to function at high temperatures the product stream contains higher fractions of high molecular weight hydrocarbons. Another object of this invention was the increase of catalyst stability with time on stream. A CO conversion of 50% was obtained after 120h on stream at 623K and 15.3 bar compared to 20% CO conversion when the support used was Ce-Zr-O.

Some inventors report on Pt-free catalyst formulations that effectively promote the WGS reaction at high temperatures, considering that Pt is an active catalyst which raises the cost of the process [134-136]. On the other hand, metals such as Co, Ru, Pd, Rh and Ni are active catalysts but cause methanation reaction (CO conversion to CH₄), a drawback that limits the utility of these metals towards the WGS reaction. Thus, the main challenge was to develop a rather inexpensive but highly selective catalyst for CO conversion towards H₂ production.

Idem et al. [134] proposed a HT-WGS reaction catalyst efficient also for the CO₂-reforming of hydrocarbons reaction (dry reforming), an important aspect of use in a hydrocarbon steam reforming catalytic technology. The catalyst mainly consists of a catalytically effective amount of Ni and/or Cu dispersed on a support. The support is a suitable mixed metal oxide prepared based on a surfactant templating method. The Ni- and/or Cu-based mesoporous supported ceria/zirconia catalysts were found to be the most effective catalysts for HT-WGS reaction. The catalysts contain about 1-10 wt% of one or more metals (Cu, Ni) dispersed on the oxidic support. For the support formulation, a first oxide in the range of 50-70 wt% was doped with a second one in the 30-50 wt% loading range. Another formulation of catalyst comprised of: (a) an oxide support comprising a first oxide selected from the group consisting of zeolites and oxides of Ce, Si, Th, Mg, Y, La, Zr, Al, Ti, Hf, Nb, Ta, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Mo, W, Re, Rh, Sb, Bi, Mn, Ga, Sr and Ba, and a second oxide selected from the group consisting of zeolites and oxides of Ce, Si, Th, Mg, Y, La, Zr, Al, Ti, Hf, Nb, Ta, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Mo, W, Re, Rh, Sb, Bi, Mn, Ga, Sr and Ba. The ratio of the amount of the first oxide to the second oxide was in the range of 50:50 (w/w) to 70:30 (w/w), where the first and second oxides are different. It was found that the bimetallic catalysts were superior when compared to the monometallic ones. The catalyst with composition 3wt%Ni-5wt%Cu/Ce₀.₇₀Zr₀.₃₀O₂ was found to exhibit the best H₂ selectivity compared to the rest of compositions investigated, where the CO conversion was found to be influenced by the Ni loading, while H₂ selectivity by Cu loading. Ni and Cu were found to promote methanation reaction at 773K. However, Cu was found to be more effective since only 200ppm of CH₄ were produced. The bimetallic system also favored CH₄ formation depending on the Ni content. The lowest average methane product composition (60ppm) was found at 673K over the 3wt%Ni-5wt%Cu/Ce₀.₇₀Zr₀.₃₀O₂ catalytic system.

Another Pt-free catalyst for producing a hydrogen-rich gas is reported in the US7160534 patent (Hagemeyer et al. 2007) [135]. Many catalysts have been developed for temperatures higher than 723K and pressures above 1 bar, while their activity was found to be low for temperatures lower than 723K. According to the method invented, a CO-containing gas such as syngas (mixture of CO/H₂) contacts a Ru-Co-based WGS catalyst in the presence of water at a relatively low-temperature (T< 723K) to produce a hydro-
gen-rich gas. The disclosed catalyst (Ru-Co) is formulated from: a) Ru metal, its oxides or mixtures of them, b) Co, Mo, their oxides or mixtures of them, and c) at least one of Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, and Eu oxides and mixtures of them. The WGS catalyst may be supported on a carrier, such as any member or a combination of alumina, zirconia, titania, ceria, magnesia, lanthana, niobia, zeolite, perovskite, silica clay, ytrria and iron oxide.

Hagemeyer et al. [136] trying to improve the above mentioned patent have reported the development of noble metal-free, Ni-based catalyst formulations that effectively promote the WGS reaction at T< 723K. The catalyst also contains at least one of Ge, Gd, In, Sn, Te, Pb, whereas the support of the catalyst could be alumina, ceria, zirconia, titania, or magnesia. The same group has also reported Pt, Rh and/or Fe-containing catalyst formulations for WGS reaction at temperatures lower than 723K [137], whereas metals such as Co, Ru, Pd, Rh, Ni were reported to be active towards the WGS reaction but at the same time promote also the undesired methanation reaction of CO. Table 4 provides a summary of important recent patented supported metal catalyst compositions related to the use of ceria as support or additive for the High-Temperature Water-Gas Shift reaction.

### 4.4. Fuel Cells Applications

As stated in section 3.1.4, fuel cell-based technologies for power generation mostly utilize hydrocarbon-based fuel processors, where the hydrocarbon fuel is converted (reformed) into a H₂-rich gas stream. However, through the reforming process about 10 vol% CO is also produced which is a very high value for the poisoning tolerance of the anode electrodes of fuel cell. Improvements of conventional water-gas shift catalysts becomes, therefore, a very important task, and this has already been discussed in US9708334 patent (Sederquist et al. 1997) [138], where a catalyst based on Cu/ZnO and alumina is presented. However, such catalyst compositions have the limitation that they must be treated with H₂ in order to get reduced prior to use, where precautions should be taken to prevent their exposure to oxygen after operation. Exposure to oxygen can be detrimental to the catalyst in terms of sintering, loss of surface area and decreasing activity. These requirements demand a special shutdown purge of the catalyst and an inert atmosphere, which both result in complexity and cost for the fuel cell plant operation. Although noble metal supported catalysts (e.g., ceria used as support) have exhibited promotional effects towards the WGS reaction, there was not yet sufficient activity to allow reasonable sizing of reactors. In addition, the high steam concentration used under WGS reaction conditions leads to sintering of ceria support. US20030007912 patent (Silver 2003) [139] reports on a catalyst suitable for reducing the amount of carbon monoxide in the process gas for fuel cell applications, addressing the aforementioned issues of catalyst pre-conditioning. The catalyst composition consists of noble metal supported on mixed metal oxides, including at least both ceria and zirconia. Cerium is present in the range 30-50 mol%, whereas zirconium in the 50-70 mol% range. Additional metal oxides may also be present. Use of the particular catalyst

### Table 4. Brief Description of Important Recent Patents Related with Ceria-based Catalysts for the HT-WGS Reaction.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Support</th>
<th>Additives/ Promoters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt, Rh, Pd</td>
<td>ZnO (MgO, CaO, SrO, BaO)</td>
<td>CeO₂ (NiO, Pr₂O₃, TiO₂, Nd₂O₃, MnO₂, Co₂O₃)</td>
<td>[123]</td>
</tr>
<tr>
<td>Pt, Pd, Ru, Ir</td>
<td>CeO₂, ZrO₂, La₂O₃</td>
<td>Y, Cs, Li, K, Mg, Sr, Ba, Ca</td>
<td>[124, 125]</td>
</tr>
<tr>
<td>Re, Pt, Rh, Pd, Ru</td>
<td>CeO₂, ZrO₂, (Ga₂O₃, Nd₂O₃, Fe₂O₃, GeO₂, W₂O₆, Sn₂O₃)</td>
<td>Na, K, Cs, Rb</td>
<td>[126, 129, 130]</td>
</tr>
<tr>
<td>Pt</td>
<td>CeO₂, ZrO₂, TiO₂, H₂O</td>
<td>Re</td>
<td>[127, 128]</td>
</tr>
<tr>
<td>Pt, Re</td>
<td>MO.₆Al₂O₃ (where, M: Ca, K, Ba, Sr, Mg, Mn)</td>
<td>CeO₂, ZrO₂, (La₂O₃, Nd₂O₃, TiO₂, Sm₂O₃, Pr₂O₃, MgO, CaO, Cr₂O₃, MoO₃, SiO₂, TiO₂, Y₂O₃)</td>
<td>[131]</td>
</tr>
<tr>
<td>Pt, Re</td>
<td>Al₂O₃, SiO₂, ZrO₂, CeO₂</td>
<td>MoO₃</td>
<td>[132, 133]</td>
</tr>
<tr>
<td>Cu, Ni</td>
<td>CeO₂, ZrO₂</td>
<td></td>
<td>[134]</td>
</tr>
<tr>
<td>Ru (Co, Mo)</td>
<td>TiO₂, Al₂O₃, SiO₂, ZrO₂, CeO₂, MgO, La₂O₃, SiO₂, Nd₂O₃, Y₂O₃, Fe₂O₃</td>
<td>Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Mo, Mn, Fe, Co, Rh, Ir, Ge, Sn, Sb, La, Ce, Pr, Sm, Eu</td>
<td>[135]</td>
</tr>
<tr>
<td>Ni</td>
<td>Al₂O₃, TiO₂, ZrO₂, CeO₂, MgO</td>
<td>Ge, Gd, In, Sn, Te, Pb</td>
<td>[136]</td>
</tr>
</tbody>
</table>
composition eliminates the requirements of prior reduction of catalyst, and minimizes the need to protect the catalyst from oxygen during operation and/or shutdown. Towards facing the same issues, US6455182 patent (Silver 2002) [140] reports on an improved catalyst (Pt/CeO₂-ZrO₂) for fuel cell applications and without the need for pre-conditioning. The catalyst activity was found to be similar to that obtained over the Cu-Zn traditional WGS catalysts. According to the inventor, the additional cost, volume, and system complexity due to the reduction/ purging/inertness requirements associated with the latter traditional WGS catalysts would be minimized in the case of use of the invented catalyst. Conventional LTS catalysts (CuO-ZnO) present relatively low activity, and due to aging, the catalyst should be replaced periodically by a fresh one. This means that CuO-ZnO catalyst is difficult to be applied in fuel cell power generation systems, where start-up and shut-down procedures are repeatedly carried out. However, this problem could be tackled by using Re supported on an inorganic oxide, such as alumina, zirconia, magnesia, niobia or zinc oxide. Cerium, yttrium, calcium, praseodymium and lanthanum oxide can be added in the support. When Pt is used, it was found that Pt of less than 0.1 wt% leads to low CO conversions, whereas Pt loadings higher than 10 wt% leads to a very high production cost. When one of the Re, Sm, Y, Cr, Ca, Zr, Ce, W, Nd metals is added in addition to Pt, CO conversion is increasing, and methanation reaction is prevented. A third metal oxide could be added such as HfO₂, La₂O₃, Nd₂O₃, PrO₃, which serves for ZrO₂ stabilization and ceria promotion, thus reducing the required reactor size.

5. CURRENT & FUTURE DEVELOPMENTS

The recent progress made in the development of heat resistant, low-cost, sulphur-tolerant and durable catalytic systems for the industrial hydrogen production has been driven by the necessity to overcome the limitations offered by the conventional catalytic materials for steam reforming (e.g., supported-Ni catalysts on alumina support), LTS (e.g., Cu-Zn) and HTS (e.g., Fe-Cr) catalysts for the water-gas shift reaction. However, many improvements are needed to be made in the catalytic systems patented so far, and new developments must be expected related to the increasingly important technology of fuel cells for power generation, which could revolutionize the energy market.

(a) Water-Gas Shift

Some of the issues regarding catalyst developments towards the WGS reaction that need to be tackled are described in what follows:

(i) Sulphur reduction to less than 0.1ppm level, since many of the so far developed catalysts still suffer from deactivation (2-10 years before replacement). However, desulphurization of hydrocarbon feedstock, mainly diesel, LPG and naphtha to such low-sulphur levels is very expensive, raising thus the operational cost, and therefore reducing the incentive for catalyst manufacturers to develop WGS catalysts that last longer.

(ii) Improvements in the activity of the catalytic systems known so far for LTS and HTS catalysts in stationary industrial facilities are not required [9]. However, if fuel cells are to make inroads in mobile applications, there is a drastic need to obtain much more active WGS catalysts, so that both their weight and volume can be reduced by a factor of at least 10 over the current best catalyst [9].

(iii) For applications to small-scale fuel cells undergoing frequent air purges, improvement of the stability of the existing catalysts to overcome deactivation with time-on-stream in realistic reformate-gas streams is required. The latter is due to metal-induced reduction of ceria, precious metal sintering after high-temperature reaction, aging of noble metal supported catalysts, and carbonate formation. In addition, deactivation found in cyclic operation, mimicking the frequent shutdowns to room temperature followed by re-start of a realistic fuel cell system should be overcome.

(iv) Future developments based on noble metal catalysts should consider their low reserves, thus their increasing high cost. Thus, for the low-temperature WGS less expensive catalytic systems should be searched for. However, as recently reported [23] high active and stable low-T WGS catalysts that contain only trace amounts of a noble metal could be an important innovation for this application.

(v) Coal gasification is a viable technology for large scale production of hydrogen from coal. However, before this technology becomes a feasible source of hydrogen with low greenhouse gas emissions, technical challenges must be overcome. One of these is the maximisation of thermal efficiency of the process, where the WGS reaction must be conducted at high temperatures in a catalytic membrane reactor downstream of the gasifier [141]. Thus, novel and cost-effective HTS catalysts must be developed.

(vi) The homogeneously catalysed WGS reaction could be considered as an alternative approach to overcome the above mentioned problems presented by the heterogeneous catalytic materials. However, according to Jacobs and Davis [9], who provided a thorough description of the work published in the open literature on the homogeneous WGS, the metal carbonyl-based catalysed processes have not been advanced in a commercial stage simply because the activities of the developed homogeneous catalysts that would satisfy industrial requirements lie only in the high-temperature range, where the ease of operation with heterogeneous catalysts makes them a clear choice for industrial use.

(b) Hydrocarbon Steam Reforming

A big challenge still remains towards the development of catalysts that would be more efficient and with longer lifetime for sulphur-tolerance hydrocarbon steam reforming without the need to further reducing sulphur content in the feedstock than what is the current practice. Similar issues are the catalyst deactivation due to coking and the efficient processes of catalyst regeneration.

In addition to catalyst deactivation due to coking and sulphur poisoning, which have not been fully clarified, other impurities contained in the reforming stream, namely: HCl,
REFERENCES

In terms of reactor design, traditional fixed-bed reactor configuration seems not to be suitable for the reforming of liquid bio-oil compounds due to their thermal decomposition and severe coking leading to deactivation. Instead, fluidized-bed configuration is successfully employed. In the latter case, attrition concepts should be considered in catalyst design. Micro-channel reactors show promising properties for mobile hydrocarbon fuel processing, such as process enhancement through high heat and mass transfer, resulting to smaller reactor volumes with high efficiency. Furthermore, catalyst characteristics for such kinds of reactors require high activity, minimum deactivation rates, and strong adhesion to the substrate. The micro-channel geometry proved to be beneficial for all the units employed, namely, the steam reforming reactor (minimization of heat transfer constraints), allowing thus the catalyst to operate at elevated temperatures (kinetic limit region), and the water-gas shift reactor, where through exceptional temperature control, reduction of catalyst volume is achieved.

In the case of Absorption Enhanced Reforming (AER), one of the main issues that should be addressed is the stability and regeneration of CO₂-absorbent material. A suitable absorbent material should combine a suite of properties, such as stability, regeneration capability and effectiveness. In the AER case, one of the main concerns is the mass transfer resistance between the catalyst (reaction center) and the absorbent (CO₂-absorption center). By exploiting nanoscale materials design concepts, integration of these features into one catalytic particle could be feasible, leading thus to a multifunctional catalyst. The latter remains one of the very challenging aspects in materials engineering field coming up as a near future scenario.

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CONFLICT OF INTEREST

The authors of this review are not in any conflict of interest.

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Ceria-based Catalytic Materials for Hydrogen Production Via Hydrocarbons

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