

ADVANCES IN NON-NOBLE-METAL CATALYSTS FOR REFORMING AND CONVERSION OF HYDROCARBONSS

*A technical investigation commissioned by the members of the
Catalytic Advances Program (CAP)*

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SCOPE OF REPORT

- ▶ In the catalyst selection a special emphasis is put on the catalyst synthesis and properties, and *in situ* characterization to elucidate the active sites and surface mobility of metals during reforming.
- ▶ Coking mechanisms and possible gasification of carbonaceous species occurring on oxygen defects have been studied and for example diffusion rates of oxide ions have been determined.
- ▶ Novel ideas, such as the use of renewable energy sources for reforming, novel energy sources such as concentrated solar power, electrified reactors, photocatalysis, plasma, solid fuel cells and the combination of reforming with separation, e.g., chemical looping and the use of membrane reactors are summarized.
- ▶ Autothermal reforming combining endothermic steam reforming with exothermic partial oxidation has been considered as an alternative for steam reforming as it can operate at S/C ratio as low as 0.6 which along with high reforming temperatures enables larger single-train capacities. The generated syngas has low H₂/CO and high CO/CO₂ ratios.
- ▶ Important issues in hydrogen generation from methane are thermodynamic limitations and endothermicity of the reaction, requiring operation at high temperature, as well as inherent to that cracking and subsequent catalyst deactivation.
- ▶ Catalyst shape is extremely important for steam-reforming catalysts, since it influences activity and the heat transfer coefficient. The shape should be designed to maximize the heat transfer rate, and subsequently the reaction rate, and minimize the tube wall temperature. Very sophisticated shapes have been commercialized. Recent developments in steam reforming include introduction of the structured reforming catalysts in the form of thin metal foils shaped into modules.

This report discusses recent advances in hydrogen production via reforming from natural gas and naphtha as well as from some organic compounds and a special effort is put on thermodynamics, product quality, catalyst selection, its stability and industrial applicability.

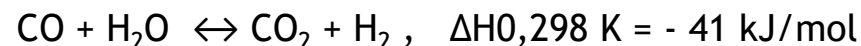
INDUSTRY DRIVERS / ECONOMICS

- ▶ Hydrogen demand is expected to increase substantially in the future. Many industries currently use large amounts of hydrogen for production of ammonia and methanol (as well as for carbon-neutral transportation fuels and power generation).
- ▶ The main hydrogen demand in U.S in 2015 was in oil refining, which requires hydrogen for sulfur removal, hydrotreatment and hydrocracking.
- ▶ Natural gas steam reforming occurring at high temperatures has been the main method to produce hydrogen during recent decades.
- ▶ The main component in natural gas is methane, thus steam reforming of methane (SRM) is often used as an equivalent for steam reforming of natural gas. This technology requires high investment costs, e.g., high-grade alloys for the catalytic tubes are needed.
- ▶ In EU hydrogen strategy several scenarios were developed for production of sufficient amounts of hydrogen. In one scenario hydrogen was supposed to be met by decentralized electrolysis.
- ▶ In an alternative scenario, the majority of hydrogen would still be coming from natural gas reforming by SRM/ATR (autothermal reforming), because natural gas has the lowest cost giving the lowest hydrogen price in comparison to hydrogen price produced via alternative routes, e.g., wind, electrolysis, solar power.
- ▶ Emerging markets have been identified in U.S. Hydrogen strategy in a long-term vision by 2050 for hydrogen utilization including transportation, construction, and power sector.
- ▶ Several application areas to accelerate hydrogen economy were also emphasized, e.g., to use at least 20% hydrogen in combustion in turbines, use reversible SOFC to produce low-cost electricity from natural gas, internal reforming combined with condensation of exhaust gases and especially enhance reforming combined with CCUS.

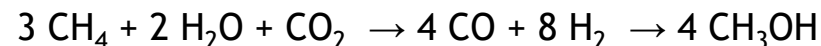
Due to the ambitious plans to decarbonize hydrogen production announced in Europe and representing the view of 17 companies several scenarios and price estimates have been made to produce low carbon and clean hydrogen.

CONVENTIONAL AND NOVEL REFORMING CATALYSTS: FOCUS ON TARGET PRODUCTS - H₂, CO, SYNGAS

- ▶ **Natural gas is mainly composed of methane**, 96% together with ethane as well as traces of hydrocarbons ranging from C₃-C₇. This method is the main technology for hydrogen production. In addition, dry reforming of methane (DRM) applies equimolar amounts of CO₂ and CH₄ as a feedstock.
- ▶ Natural gas steam reforming occurring at high temperatures, e.g., 700-1000 °C under 3 - 25 bar has been the main method to produce hydrogen during recent decades. Currently hydrogen generated from natural gas by steam or autothermal reforming has the clear cost advantages compared with hydrogen produced via alternative routes, e.g., electrolysis of water.
- ▶ **In methane steam reforming the theoretical** H₂/CO ratio is about 3 and the use of steam can suppress carbon deposition. H₂/CO ratio from SRM is considered to be too high for the Fischer-Tropsch (FT) process. The H₂/CO ratio from DRM is typically ca. 1 which is suitable for FT synthesis of long chain hydrocarbons. If high purity hydrogen is required, the hydrogen yield can be enhanced by enhancing water gas shift (WGS) reaction:



- ▶ Other methane reforming processes are bi-reforming of methane in the presence of both CO₂ and water as oxygen sources while in methane tri-reforming (TMR), water, oxygen and CO₂ are used as oxidants and the heat is produced from methane oxidation either to CO or CO₂



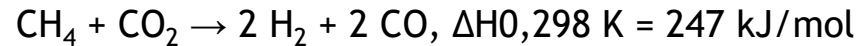
- ▶ In naphtha steam reforming, in addition to hydrogen and CO, also high amounts of CO₂ are formed. For example, high amounts of hydrogen can be obtained especially with a high steam to carbon ratio, e.g., with the ratio of 6 the hydrogen yield from heptane was 72 mol% above 650 °C while other products were CO₂ (ca. 18 mol%), and CO (ca. 4 mol%) at 650 °C under 400 kPa

A special effort in this report is put on thermodynamics, product quality, catalysts selection, their stability and industrial applicability. Specifically, the catalyst synthesis and properties, and in situ characterization to elucidate the active sites and surface mobility of metals during reforming are addressed.

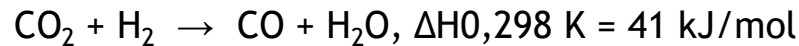
THERMODYNAMIC AND KINETIC BACKGROUND

FOCUS ON: DRY REFORMING OF NATURAL GAS, METHANE

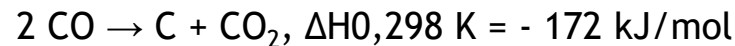
- ✓ Dry methane reforming (DRM) has been intensively studied in the recent years and some reviews (presented in this report) have been published on this topic. DRM involves highly endothermic reactions theoretically giving the H₂/CO ratio of 1.
- ✓ If the H₂/CO ratio exceeds unity, it indicates the presence of Boudouard reaction, while if CO₂ conversion is higher than that of methane, the water gas shift reaction and CO₂ reforming of methane occur simultaneously.
- ✓ Due to the harsh reaction conditions in DRM to obtain adequate conversions, high reaction temperatures should be applied, which cause challenges in the reactor material selection and energy consumption. The main challenges for the stable catalyst performance due to harsh reaction conditions are metal sintering and coking.
- ✓ In dry methane reforming high temperatures and low pressures are required for the following reaction due to high stability of CO₂.



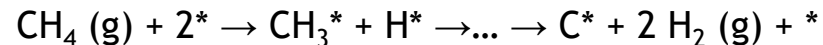
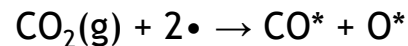
- ✓ The reaction above is also highly endothermic. In addition, the reverse water gas shift reaction (RWGS) can occur



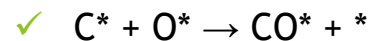
- ✓ Typically, a higher conversion of CO₂ in comparison to methane is obtained resulting in the H₂/CO ratio 1 or less. Furthermore, the methane decomposition and the Boudouard reaction, i.e., disproportionation of CO, can occur promoting catalyst deactivation.



- ✓ In DRM a stable catalyst performance requires that the rate for CO₂ activation on the catalyst surface (A.7) is equal to the rate for methane activation where the asterisk (*) refers to a vacant binding site although a CH_x* intermediate can directly be converted by an O species.



- ✓ When an equal number of C and O atoms are formed on the surface CO is formed by their recombination:



MECHANISTIC ADVANCES AND IN SITU/OPERANDO STUDIES

DRY REFORMING OF NATURAL GAS

- ✓ Density functional theory (DFT) calculations have been used to reveal reaction mechanism in DRM over Ni/CeO₂ catalysts. Initially CO₂ is activated at the vacancy site of Ni/CeO₂, while methane activation occurs on the interfacial vacancy site and the metal site, which both have high reactivity.
- ✓ CO is mainly formed by CO₂ dissociation and the remaining O* species could fill in the vacancy site or alternatively diffuse to react with CH_x* which is formed via methane dissociation. The oxygen vacancies area healed by O* after CO₂ dissociation. At the same time the metal is covered by the fractionation products originating from methane. These species are strongly bound to the metal surface lowering the reaction rate.
- ✓ In situ DRIFTS was used as a tool to study the reaction mechanism in DRM over Ni/MgO-Al₂O₃ mixed oxide catalyst. A higher intrinsic activity was observed for Ni/Mg-Al-O catalyst prepared by cation-anion double hydrolysis than over conventional Ni/MgO/Al₂O₃ prepared via co-impregnation due to the presence of ultrasmall Ni particles in the former catalyst.
- ✓ Based on these results the following reaction mechanism was proposed: CH₄ is dissociated on Ni surface producing H* and CH_x* species, where * denotes adsorbed surface species.
- ✓ CO₂ is activated on the basic support forming carbonate/bicarbonate species, which can be further transformed to formate species. These formate intermediates decompose into CO and OH*. The latter one can oxidize CH_x* producing CO and H₂, H* species can also recombine to dihydrogen. Formate species are formed via involvement of H*

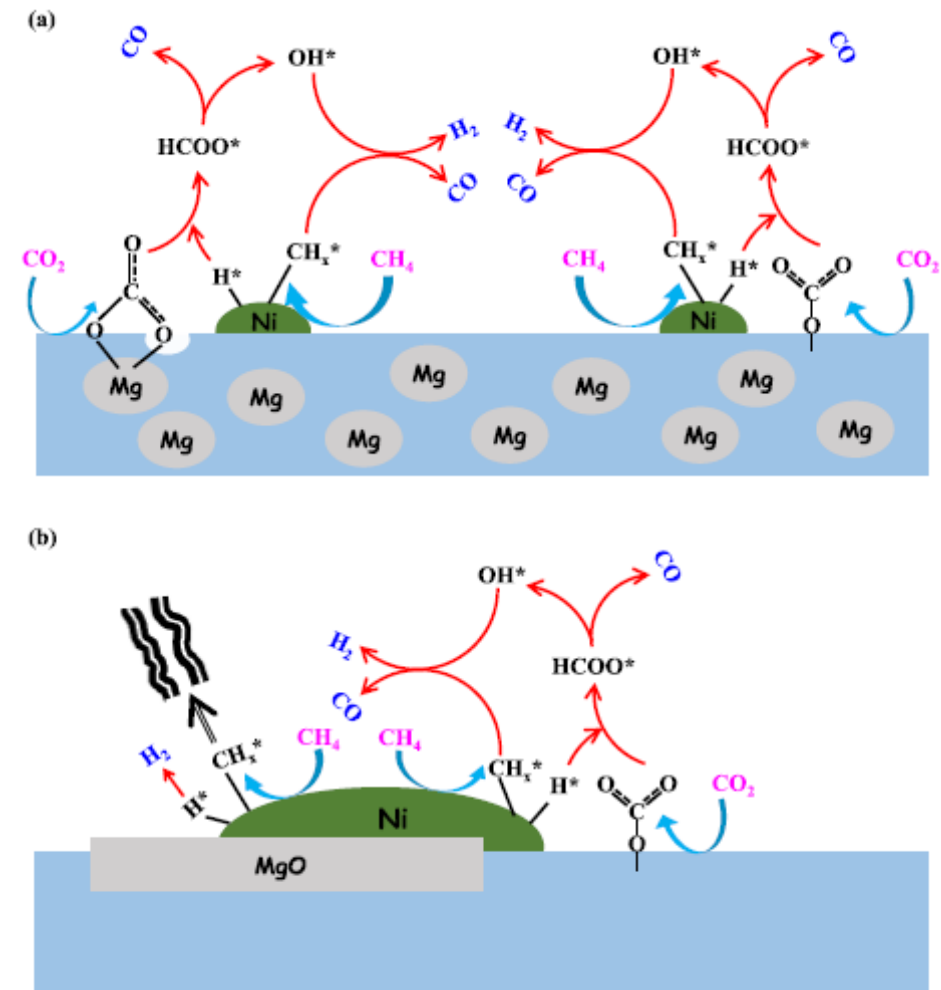


Figure 1: Possible reaction mechanism for methane reforming over a) Ni/MgO-Al₂O₃ catalyst prepared by coimpregnation, b) over Ni/Mg-Al-O prepared via cation-anion double hydrolysis method. Notation: * denotes the adsorption state. Source: Guo et al., 2020

NOVEL ENERGY INPUT FOR REFORMING

FOCUS ON: MICROWAVE ASSISTED REFORMING

Microwave assisted methane reforming has attracted a lot of attention since ferromagnetic alloys can absorb microwave irradiation and gasification of carbonaceous species can be enhanced under microwave irradiation. Recently, a review was published on microwave-assisted methane reforming covering several studies applying microwave heating for DRM and BRM.

Microwave heating was used in DRM when using CoMo/Al₂O₃ as a catalyst and different Co/Mo ratios as well as microwave powers were tested. It was demonstrated that the monometallic Co and Ni supported on alumina were inactive, while for bimetallic catalysts the methane conversion increased with increasing Co/Mo molar ratio and that the optimum molar ratio of Co/Mo giving the highest methane conversion was 2. CO₂ conversion increased in an analogous way with increasing the Co/Mo molar ratio.

When DRM reforming was performed at 700 °C over Ni/Al₂O₃ catalyst using 2:1 CO₂ to methane ratio conversion of methane decreased in 6 h TOS from 92% to 42%. Thereafter the thermal heating was changed to the microwave heating and at the same time CH₄ conversion increased to ca. 70% in 2 h TOS and was stable for the subsequent 2 h. This result indicates that both catalytic activity and stability were enhanced via applying the microwave heating.

NOVEL ENERGY INPUT FOR REFORMING

FOCUS ON: PLASMA REFORMING WITH DIELECTRIC BARRIER DISCHARGE

Several methods have been investigated in plasma assisted methane reforming including thermal plasma and cold plasma. The production of thermal plasma requires high pressure and a high-power input. In thermal plasma-assisted DRM both gas and electrons are at high temperature corresponding to the equilibrium process for DRM. Due to these reasons non-thermal plasma (NTP) has been recently under investigation, especially for DRM (see below). A recent review on the use of a non-thermal catalytic dielectric barrier discharge reactor in DRM gives a very comprehensive picture of the mechanism.

FOCUS ON: PLASMA PHOTOCATALYSIS ASSISTED REFORMING C BARRIER DISCHARGE

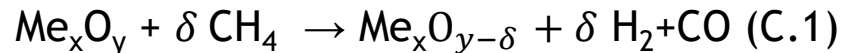
Plasma-assisted photocatalysis in DRM was investigated in. In their work a spark discharge reactor with different perovskite type photocatalysts was investigated using CH_4/CO_2 ratio of one. The highest hydrogen selectivity, 83.4 % was obtained over NiTiO_3 catalyst at a high GHSV of 170,000 h^{-1} using 16 kV input voltage and frequency of 20,000 Hz when methane and CO_2 conversion were 48.5% and 48.5%, respectively. The corresponding energy efficiency and the carbon balance were 14.9% and 87.1%, respectively. The hydrogen production was also promoted by a high feeding flow rate, because it is formed by an exothermic recombination of hydrogen, which requires an interplay of the quartz tube, electrodes and the photocatalyst. The opposite is valid for CO production, i.e., it is formed in higher amounts at lower GHSV. These results can be explained by the formation mechanism of CO, e.g., it is formed from CO_2 and alternatively by dehydrogenation of COOH , CH_2O and CHO radicals. Furthermore, a synergy was found between plasma and photocatalysis, even if the photocatalytic effect alone was rather low. DRM only in plasma produced hydrogen with a selectivity of 74.4% at 1700,00 h^{-1} , while in the presence of plasma and NiTiO_3 hydrogen selectivity was 88.4%. It was interesting to observe that during plasma-assisted photocatalytic DRM the particle size of NiTiO_3 decreased from 38 nm for the fresh one to 29 nm in the spent one. This result was explained by the electron bombardment occurring during plasma reforming.

NOVEL PROCESS CONFIGURATIONS

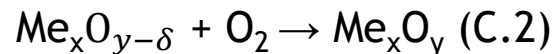
Novel process configurations, for example combination of reforming with separation, have recently been studied intensively. For separation adsorbents and membranes have been applied with an objective to shift the reaction equilibrium and achieve high conversions. These novel process configurations can potentially improve methane conversion and produce highly pure hydrogen as well as facilitate the use of moderate temperatures and pressures especially in steam methane reforming.

Chemical Looping

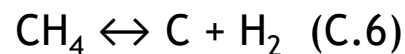
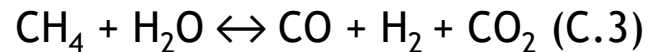
In sorption enhanced chemical looping-steam reforming (SE-CLR) partial oxidation of the lattice oxygen in oxygen carrier occurs for example over Mg promoted Fe/Al₂O₃:



followed by reoxidization of the reduced oxygen carrier (Hafizi et al., 2016)

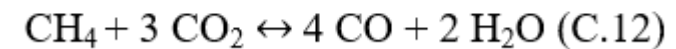
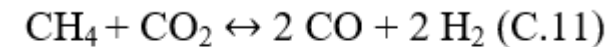


In addition to these reactions also CO oxidation and decomposition of methane can occur:



Membrane Reactors

Membrane reactors have been studied already for two decades and their use in SRM is summarized in the recent review. Membrane reactors are used to enhance the rate in e.g., DRM, in which methane dissociation has been stated to be the rate limiting step. Such acceleration is because of a transport of reactants/products through the membrane by applying a driving force, such as pressure, temperature or concentration gradients.



FOCUS ON: GLYCEROL & METHANOL

GLYCEROL

- The increase in glycerol amounts obtained from transesterification in the global market from increased biodiesel production has led to an excess of this chemical. In converting vegetable oils into biodiesel, approximately 10% (w/w) of glycerol is produced as a by-product
- Several recent reviews on glycerol reforming over non-noble catalysts explored process optimization, catalysis, thermodynamics, kinetic modelling, exergy, energy and techno-economic analyses, environmental performance, and computational fluid dynamics (CFD) simulations.

METHANOL

- Methanol is the most ideal hydrogen carrier produced from renewable energy sources since it has a high carbon to hydrogen ratio (1:4). The number of publications with methanol reforming has been increasing every year along with a number of the publications focusing on on-board application grown almost by 30% in last 5 years. With the breakthrough of carbon capture and storage (CCS) technology, methanol can be further used in renewable energy networks as a representative of synthetic fuels to achieve the final goal of carbon neutrality.
- Fasanya et al. (2019) used zinc oxide nanorods, developed hydrothermally on the cordierite surface, loaded with copper and tested as catalysts for SRMe to overcome conventional disadvantages of sintering and poisoning of the catalyst. The effect of temperature, methanol content, and the particle size on the reforming reaction was examined. For reaction temperatures between 180 and 230 °C, hydrogen was formed with 98% selectivity while there was absolutely no CO. Above 300 °C, coke formation and catalyst deactivation were noticed.
- Kuo et al. (2019) designed Cu-Fe/silicate mesoporous catalysts by concurrent mixing of sodium hydroxide and the metal-ion solution to sodium silicate solution, followed by hydrothermal treatment under alkaline conditions. During this treatment, the amorphous metal-silicate was transformed into a mesoporous structured Cu-Fe/silicate catalyst. This catalyst demonstrated more than 99% conversion of methanol within an hour at around 180 °C.

FOCUS ON: CARBOXYLIC ACIDS / ACETIC ACID

CARBOXYLIC ACIDS

- Complexity of bio-oil and behavior of organic compounds, originating from their different structures and functionalities, make the direct steam reforming of bio-oil rather challenging. Among various organics in bio-oil, carboxylic acids are one of the most important fractions with the concentration of 5-19 wt% (Kumar et al., 2019).
- Understanding the reaction behavior of carboxylic acids during steam reforming could provide useful information for optimizing the process of steam reforming of bio-oil. Acetic acid is the main carboxylic acid in bio-oil, although there are also many other acids in bio-oil, including formic, propionic, butyric acids, etc.

ACETIC ACID

- Acetic acid is one of the major fractions (concentration up to range 30% by wt.) of bio-oil which consists of many other groups of oxygenated hydrocarbons such as aldehydes, ketones, alcohols, phenols and guaiacol. Acetic acid may be used safely for hydrogen production as it is non-flammable and can be easily obtained by fermentation. For this reason, acetic acid is often selected as a model compound for bio-oil for studying hydrogen production via reforming.

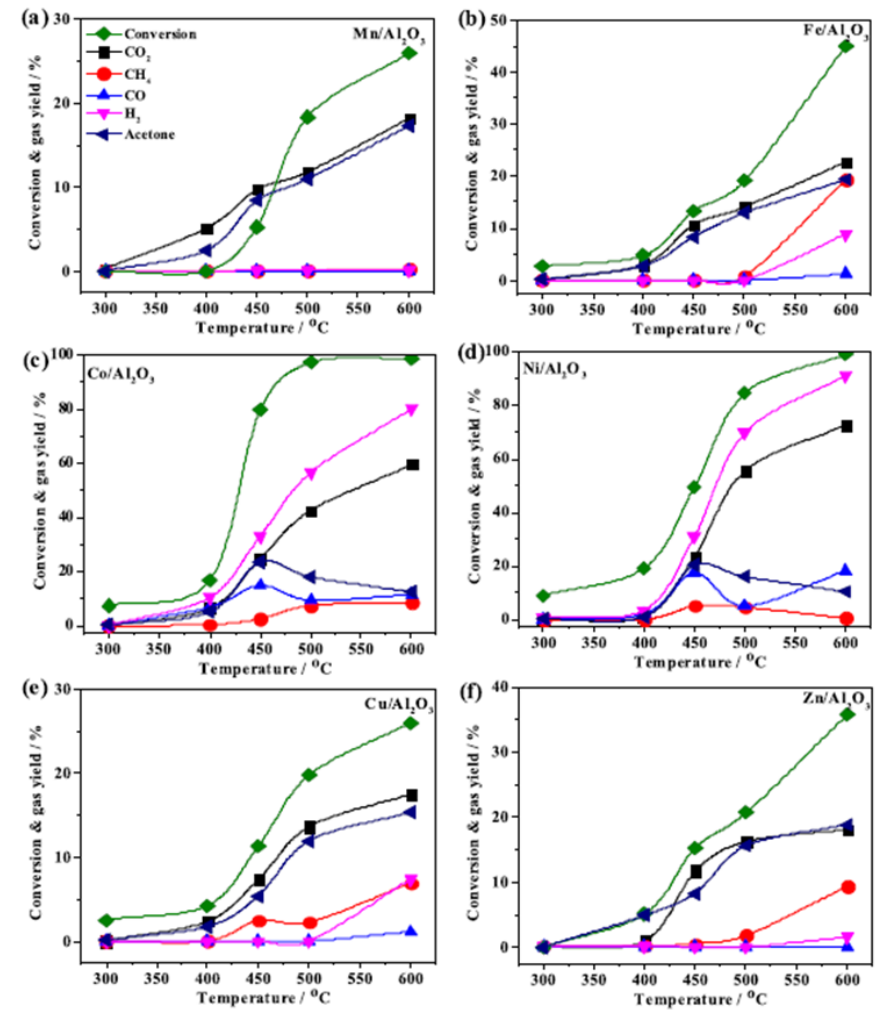


Figure 3.19. Steam reforming of acetic acid over supported metal catalysts. Reaction conditions: S/C = 5; LHSV = 12.7 h⁻¹; P = 1 atm. Source: Li et al., 2020d

REMAINING HUDRLES & FUTURE PERSPECTIVES

- ✓ One of the big challenges for dry reforming is carbon formation under the conditions when the stoichiometric ratio between methane and carbone dioxide is used. Subsequently high severity CO₂-reforming has been commercialized rather than the pure dry methane reforming. The catalysts for such reforming are similar to those for steam reforming.
- ✓ In this report, recent advances in hydrogen production via reforming from natural gas and naphtha as well as from some organic compounds are discussed based on papers published by researchers working predominantly in academia. Among the organic compounds the emphasis was primarily on glycerol, a by-product of biodiesel manufacturing.
- ✓ A special effort in this report is put on thermodynamics, product quality, catalysts selection, their stability and industrial applicability. Specifically, the catalyst synthesis and properties, and in situ characterization to elucidate the active sites and surface mobility of metals during reforming are addressed. In addition, the reaction mechanism can be revealed via isotopic labelling experiments and in situ studies. As coking and possible gasification of carbonaceous is very important for reforming reactions the mechanisms of both processes and types of coke are overviewed.
- ✓ Finally, some novel ideas about the process technology, such as the use of renewable energy sources for reforming, or novel energy sources including concentrated solar power, electrified reactors, photocatalysis, plasma, solid fuel cells and the combination of reforming with separation, e.g., chemical looping and the use of membrane reactors, are summarized.

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