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Low temperature steam reforming catalysts for enriched methane production

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Abstract Methane steam reforming (MSR) is still the most competitive process for the production of hydrogen, due to the available technology and low cost. A possible shortcut to the “hydrogen economy” is based on enriched methane (EM), a gas mixture composed by hydrogen and methane, which could be employed as a fuel by exploiting existing technologies and infrastructures, with great improvement in emissions reduction. EM can be directly obtained by low temperature MSR, due to the endothermic character of the reaction, which is usually carried out at high temperature to obtain high methane conversion. An important aspect of this process is the choice of the catalyst, which should ensure the required activity, together with stability towards deactivation. A short review of the state-of-the-art catalysts for MSR is provided, with focus on both the active phase (mainly supported Ni particles) and the oxidic support properties. The attention is then focused on the current research on low temperature catalysts, including some hints to SR of oxygenated feedstocks (ethanol, glycerol, etc), where Ru and Rh are often employed. In this context, the importance of the support is underlined, especially to improve the stability towards deactivation. The attention is focused on the most studied low temperature MSR catalyst Ni/CeZrO₂, with particular attention to the structural and surface properties of both active phase and support, which strongly influence the catalyst performances.

1 Introduction

1.1 Enriched methane as a possible shortcut towards the hydrogen economy

Enriched methane (EM) is a gas mixture composed by hydrogen and methane, also known as hydromethane. Among the many H₂ mixtures employed as fuels or in the chemical industry (such as “syngas” or “coal gas”) EM and H₂ enriched natural gas (H₂-NG) have gained increasing importance, as testified by the commercialization in the USA of Hythane®, a mixture of 20% H₂ and 80% NG. The reasons for the growing attention to EM are related to the possibility to employ it as fuel in traditional NG internal combustion engines (ICE), without the need of expensive technological modifications.

In fact, the last decade enthusiasm for the development and potentialities of hydrogen-based fuel cells (FC) has dwindled, due to the technological issues related to the managing and reliability for on-board applications. Since these aspects are still challenges for the scientific community, the technological maturity of FC is unfortunately still far from being reached. Another possibility to pursue the so-called “hydrogen-based economy” (a societal model based on the use of pure hydrogen as energy vector) is to employ it as fuel in ICE. However, the use of pure hydrogen in ICE, though fascinating, is limited by several drawbacks. These include the low energy density of hydrogen, which would result in a low mileage, and the intrinsic high flame temperature, which could improve the engine efficiency but also NO_x emissions. From the technological point of view, important aspects are the necessity to design *ad-hoc* engines (in relation to high pressure and temperature) and the still open question of on-board hydrogen storage, with related safety issues.

Most of the described issues could be overcome by the employ of hydrogen enriched mixtures in NG ICE vehicles. From the environmental point of view NG vehicles are up to now one of the best solutions, thanks to reduced emissions of particulate matter and gaseous products. NG, which is mostly composed by methane (from 85 to 98%) is characterized by a H/C ratio of 3.5-4.0, which is much higher with respect to diesel (2.1-2.2) and gasoline (2.2-2.4). This is important, in relation to the increasing urgency in the need to reduce CO₂ emissions. A further improvement in this line is the use of hydrogen (10-30%) as an additive to NG, resulting in H/C ratios higher than 4.2. This could result in an improvement of the engine efficiency with the simultaneous reduction of CO, CO₂, NO_x and unburned emissions [1-8]. Another important

aspect is the possibility to use existing NG ICE technologies and NG pipeline for mixture supply. Thus, among the commercial claims of Hythane® Company LLC for the use of their H₂-NG mixture (5-7% hydrogen) we can mention: i) a reduction of CO and NO_x by 50%; ii) low capital and operating costs; iii) cheapest way to meet new emission standards.

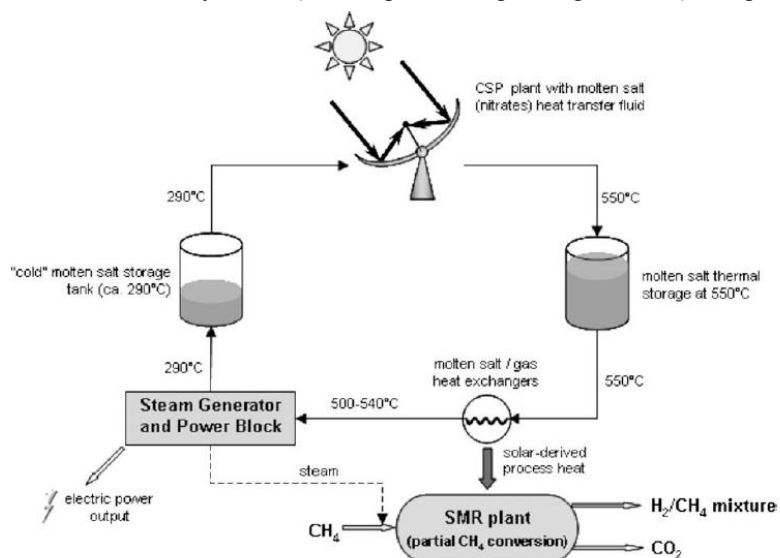


Fig. 1. Simplified scheme of CSP plant and molten salt loop, coupled to SR and electrical power generation plants. Reproduced from Ref. [9] with permission from the International Association of Hydrogen Energy.

It is thus not surprising that the feasibility of the EM approach has been proved in several international research centers by on-road tests [2, 7, 10, 11]. On the basis of an energy and environmental sustainability analysis, Villante and Genovese [2] pointed out the gain in energy efficiency and CO₂ emission reduction when passing from NG to EM blends with H₂ concentrations ranging from 5 to 25%. However, the process efficiency (and global CO₂ emission) is strongly dependent on the method employed for hydrogen production [2]. Accordingly, De Falco et al. [12] recently discussed a solar low-temperature steam reforming (SR) process for the production of EM, by exploiting the solar energy stored in a Molten Salt stream heated up by a Concentrating Solar Plant (Fig. 1) (MS-CSP). The work demonstrated the feasibility of the technology and the good match between a solar plant and an endothermic chemical process able to exploit solar energy to produce hydrogen.

1.2 Low temperature steam reforming for enriched methane production

One of the most extensively employed processes for hydrogen generation (together with NG gasification) is SR, in that about 95% of worldwide hydrogen is currently estimated to be produced through these processes from fossil fuels [13-16]. The process mainly employs NG (85-98% of methane), even if other hydrocarbons could be employed, such as propane [17], butane [18], gasoline [19], naphta [20] and liquefied natural gas (LNG) [21, 22]. More recently many SR processes of oxygenated feedstocks such as methanol, ethanol and glycerol are being investigated [23-30]. The competitiveness of NG SR is clearly related to costs and availability of existing technologies with respect to more environmentally friendly alternatives for “renewable hydrogen” [31, 32].

Methane steam reforming (MSR) is based on the following reactions:



Where the SR step is the first, highly endothermic, while the second exothermic step is Water Gas Shift (WGS), producing a further amount of hydrogen in the conversion of CO to CO₂. Due to endothermic character of the SR step, the process is usually carried out at 1073-1273 K, in order to achieve high hydrogen yield (methane conversion > 90%) [33,

34]. The gas produced in this process usually contains 70-80% of hydrogen, with a mixture of CO, CO₂, H₂O and CH₄, so that purification processes are necessary. One of the main issues is CO₂ sequestration, which is usually carried out by CCS (Carbon Capture and Sequestration) techniques, with an important energy consumption and environmental impact [2]. This implies that there is a large room for maneuver to improve both the energy efficiency and the environmental impact of SR processes.

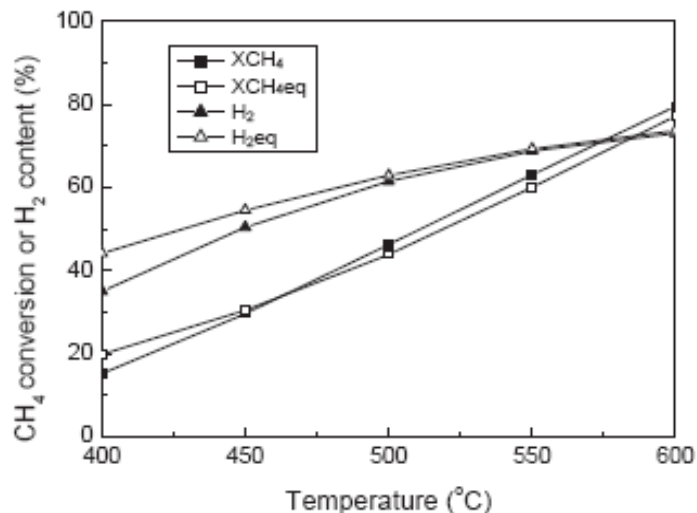


Fig. 2. Equilibrium values for CH₄ conversion and H₂ content in low temperature MSR (hollow symbols). Experimental values (solid symbols) were obtained at GHSV = 20000 mL/g_{cat}·h with a Ni/CeZrO₂/θ-Al₂O₃ catalysts. Reproduced from Ref. [35] with permission from the Korean Chemical Society.

One main parameter for improving the energetic sustainability of SR processes is the reaction temperature. Roh and Jun [35] showed that low temperature MSR is thermodynamically and experimentally possible for the generation of H₂ for fuel cells. As pointed out by De Falco et al. [9, 12], reduction of the process temperature around 773-873 K would allow the coupling to MS-CSP technologies, resulting in an important improvement of the process energetic and environmental sustainability.

Clearly, due to the endothermic character of the process, a low reaction temperature causes a decrease in methane conversion, as directed by thermodynamics (Figure 2). This implies the direct formation of a hydrogen-enriched methane mixture (EM) (Fig.3). An additional advantage of this approach is due to the fact that it is not necessary to separate the produced hydrogen from methane, avoiding the installation of expensive separation units. However, a separation unit for CO₂ removal cannot be avoided.

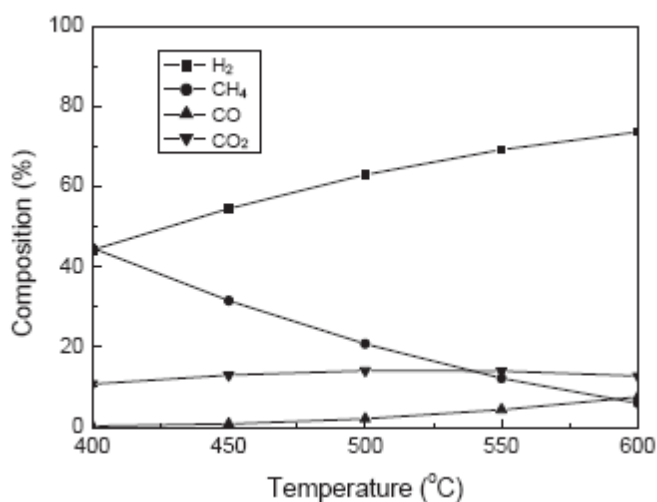


Fig. 3. Product gas composition (dry basis) as a function of reaction temperature for MSR on a Ni/CeZrO₂/θ-Al₂O₃ catalysts. Reproduced from Ref. [35] with permission from the Korean Chemical Society.

2. Catalysts for steam reforming processes

2.1 Active phases and promoters

MSR process is traditionally carried out by employing catalysts based on Ni particles supported on ceramic oxides such as Al_2O_3 , MgO , MgAl_2O_4 spinels or mixtures of these oxides [16, 20, 33, 36-38]. The choice of the support is very important since it has been reported that the metal could be inactive on inert supports [34, 39]. Other active metals were tested, including transition metal ions (Fe and Co) [40, 41] and noble metals (Ru, Rh, Pd, Pt and Ir) (Fig. 4) [42-46]. Usually, Ni and noble metals based catalysts (particularly Ru and Rh), show good activity also at relatively low temperature [34, 46, 47], and they are often employed as catalysts for SR of oxygenated feedstocks [44, 45, 48-50]. The main drawbacks, especially when Ni-catalysts are employed, are related to deactivation processes due to sintering of Ni particles and/or carbon deposition [17, 51-56].

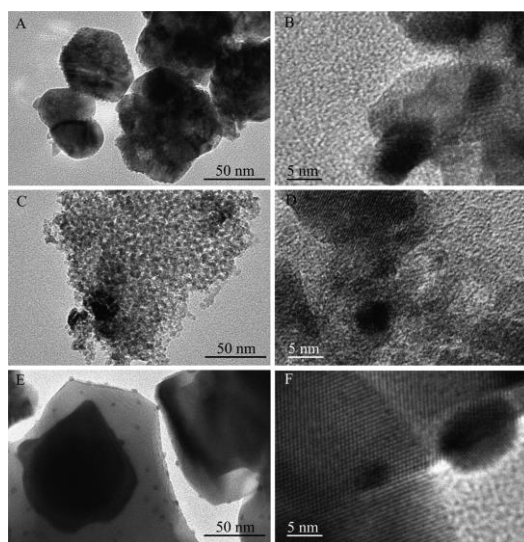


Fig. 4. TEM images at various magnifications of 1.5% Rh/CeO₂ (A and B), 1.5% Ru/Al₂O₃ (C and D), and 1.1% Pt/CeO₂ (E and F) catalysts. Reprinted with permission from Ref. [42]. Copyright (2013) American Chemical Society.

The problem of Ni particles sintering is often related to the severe conditions of the “classical” SR process (temperature around 1073-1273 K and vapor pressure up to 30 bar), which are required to shift the reaction towards product formation [34, 57]. These conditions lead to the formation on the industrial catalysts of relatively large Ni particles (20-100 nm), with related loss in surface area and activity. Direct information on the mechanism of Ni sintering could be provided by *in situ* transmission electron microscopy (TEM) (Fig. 5) [58, 59]. In Ref. [59] the authors tried to explain the different conclusions obtained in the literature with the same *in situ* technique. By studying a Ni/MgAl₂O₄ catalysts very similar to the industrial one they pointed out that very fast Ostwald ripening of the smallest Ni particles is observed at the early stages, while migration and coalescence most clearly appear at later stages of sintering, when the smallest particles had disappeared [59].

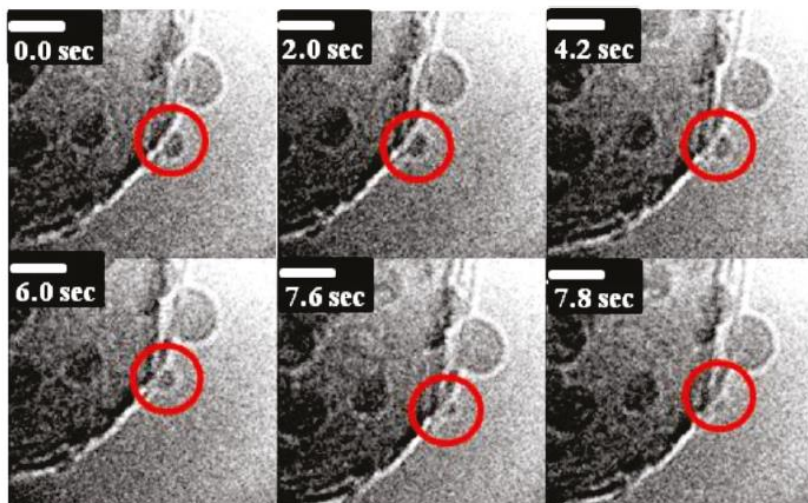


Fig. 5. TEM time-lapse image-series of a Ni/MgAl₂O₄ catalyst imaged in a H₂/H₂O (3.6 mbar) atmosphere at 1023 K, showing the disappearance of small particles of Ni and the growth of larger ones (scale bar 5 nm). These observations are characteristic of Ostwald ripening. Reprinted with permission from Ref. [58]. Copyright (2011) American Chemical Society.

The formation of carbon deposits could instead cause blocking of the reactor and disruption of the catalyst. Deposited carbon could have different structures depending on the catalyst and the reaction conditions, embedding or encapsulating Ni particles (Fig. 6) [60, 61]. This could be explained by the diffusion of surface carbon atoms (selectively adsorbed on reactive step sites) to subsurface octahedral sites forming graphene islands [62].

The high mechanical strength of carbon filaments (“whiskers”) can cause the removal of active phase particles from the support. This drawback could be minimized by modifying the steam-to-carbon (S/C) ratio of the reaction mixture. This however leads to a restriction in the process parameters and a lower H₂/CO ratio in the products [34, 57].

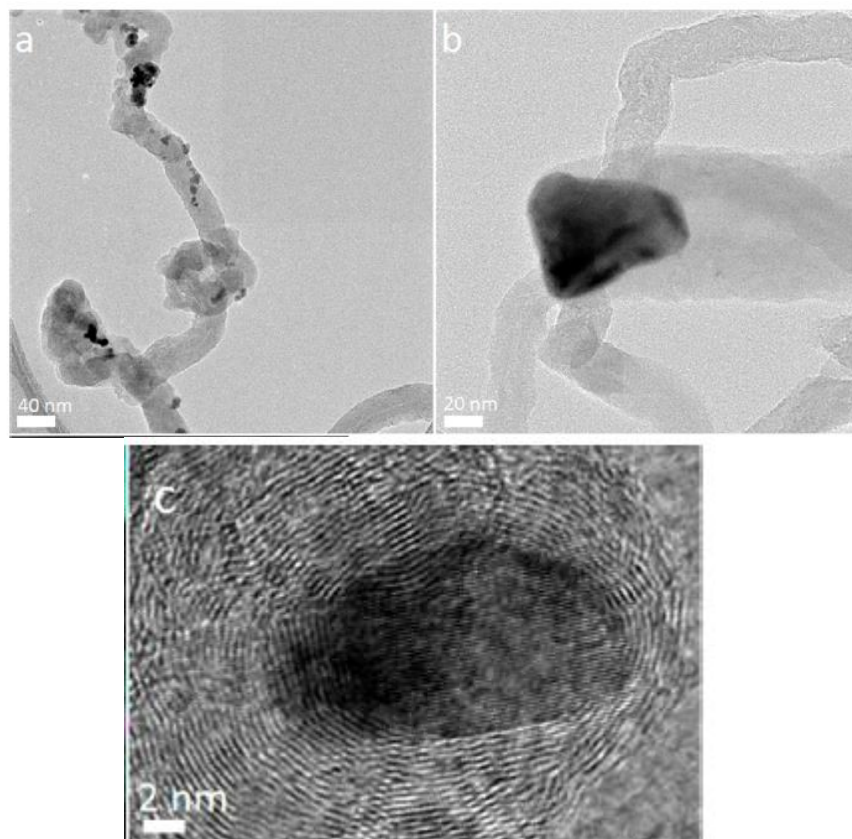


Fig. 6. TEM micrographs of a Ni/CeO₂ catalyst showing (a, b) carbon fibers embedding Ni particles and c) a Ni or NiO particle encased in graphitic carbon. Adapted with permission from Ref. [61]. Copyright (2013) American Chemical Society.

Different promoters were proposed to improve the catalyst stability toward deactivation [63]. These include alkali and alkali-earth metal ions (potassium and/or calcium) [48, 64, 65], or metallic/bimetallic precursors (Ag, Au, Cu, Sn, W, Re, etc.) [19]. The positive effect of additives such as potassium, sulfur or gold towards carbonization was explained by their binding to reactive step surface sites, thus removing the nucleation sites for the growth of graphitic filaments [36]. As for metallic systems, the promoters could also form alloys with Ni, and the change in reactivity could be related to electronic and/or “ensemble” (distribution and type of reaction sites) effects (Fig. 7) [1, 66].

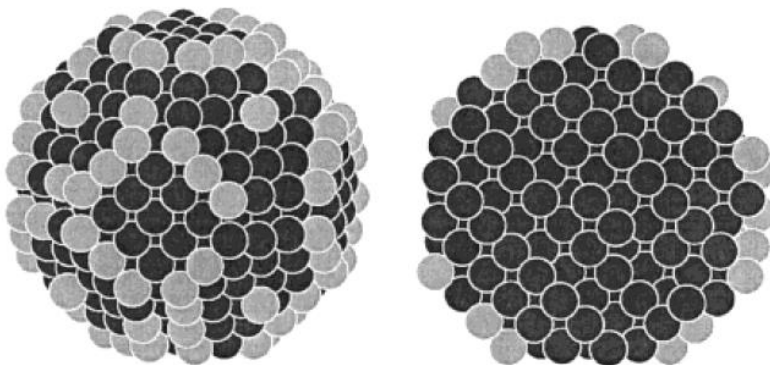


Fig. 7. Snapshot from a Monte Carlo simulation of a Au/Ni nanoparticle consisting of 100 Au atoms (light) and 583 Ni atoms (dark), with an outer diameter of 2.6 nm. Projected (left) and sliced through the centre of the particle (right) snapshots

show the formation of Au as a surface alloy at the surface of Ni cluster, with preferential binding to step sites. Reprinted with permission from Ref. [66]. Copyright (2001) American Chemical Society.

A similar mechanism was proposed for boron as a promoter, showing positive effects on both coke formation and activity [62]. This was explained on the basis of a similar chemisorption preference of boron and carbon for Ni, so that boron can selectively block step and subsurface Ni octahedral sites. This would reduce the diffusion of carbon to the subsurface sites and subsequently to the Ni bulk (Fig. 8) [62, 67].

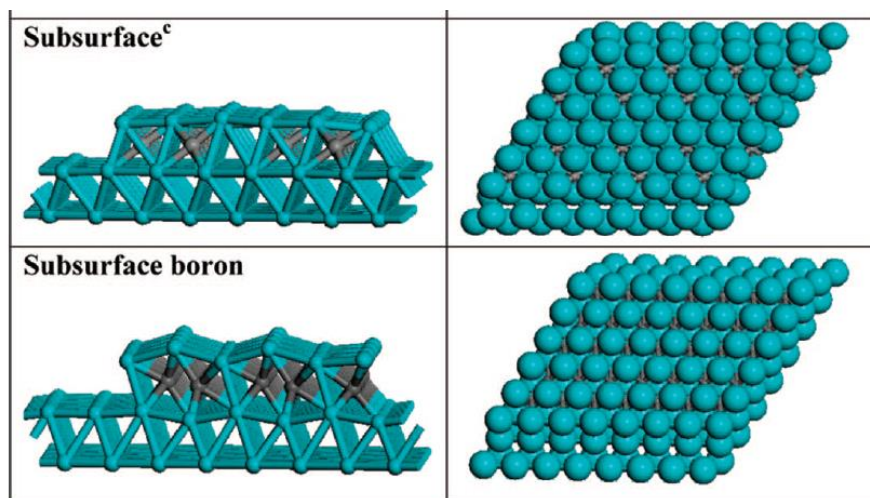


Fig. 8. Structure of a Ni (111) surface with subsurface carbon (top) or boron atoms. Small gray balls indicate carbon and boron atoms. Adapted with permission from Ref. [67]. Copyright (2009) American Chemical Society.

2.2. Influence of the support on the performance of the active phase

Apart from the use of promoters, the choice of the support and the methodology employed for the deposition or growth of Ni particles are of fundamental importance to improve stability and performances of SR catalysts. Many aspects of the support surface chemistry can influence at the same time reaction temperature and stability, both in terms of Ni particles aggregation and carbon deposition. For instance, Matsumura and Nakamori [33] compared the performances of Ni supported on Al_2O_3 , SiO_2 and ZrO_2 for MSR at low temperature, and proposed the important role of surface hydroxyl group in the activity of the Ni/ ZrO_2 catalyst. The surface acidity of TiO_2 , ZrO_2 and SiO_2 supports (Lewis or Brønsted as silanols and titanols) was also taken into consideration for the low temperature steam reforming of glycerol [68]. Moreover, the same authors explained the difference in reactivity on the basis of the metal-support interaction [68], which strongly depends on the support nature and on the preparation procedure [69-72]. In particular, the stronger the interaction, the more stable the metallic Ni clusters, which in turn lead to a higher catalytic activity and stability [68]. A strong metal-support interaction (SMSI) was also proposed for Ni/ CeZrO_2 catalysts, where some parts of NiO were proposed to incorporate in the CeZrO_2 support, thus suppressing Ni clustering and deactivation [73].

Besides chemical composition and structure, textural properties could also play an important role in improving the performances of SR catalysts. Namely, the employ of mesoporous materials as supports is steadily growing, thanks to the intrinsic advantages of this class of materials, such as large specific surface area and available volume, improving reactants and products diffusion. For instance, many papers were recently reported by Seo et al. [21, 22, 74-80] about the use of mesoporous Al_2O_3 as support for Ni particles in LNG SR. The authors studied the performances of different Ni/ Al_2O_3 mesoporous catalysts, including aerogels [22, 76] and xerogels [81]. They focused on the preparation procedures to obtain high surface area porous alumina by precipitation/co-precipitation [77, 79], sol-gel [81, 82] and surfactant assisted synthesis [21, 78, 80]. For instance, a Ni/ Al_2O_3 catalysts prepared by a non-ionic surfactant-templating method showed higher activity and stability with respect to a reference material based on commercial Al_2O_3 (Fig. 9) [21]. This was explained with SMSI and greatly enhanced Ni dispersion and surface area, thanks to the formation of a surface nickel aluminate.

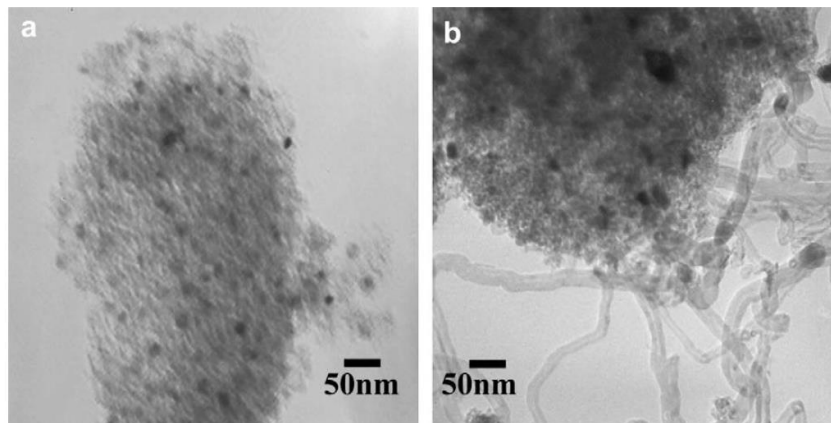


Fig. 9. TEM images of two Ni/Al₂O₃ catalysts prepared by impregnation on a) mesoporous alumina prepared with non-ionic surfactants and b) commercial Al₂O₃ (Degussa). The images were taken on catalysts after 1000 min reaction in LNG SR at 873 K. In the sample prepared by commercial support, nickel was highly sintered and filamentous carbon was formed during the reaction. Reprinted from Ref. [21] with permission from the International Association of Hydrogen Energy.

With a similar philosophy (aimed at increasing of Ni dispersion and surface area) Ni-based catalysts on mesoporous zirconia were developed and tested in methane dry reforming [83-86]. In this case the obtained specific surface areas were high (around 150 cm²/g) with respect to classical ZrO₂ supports, but sensibly lower with respect to what obtained with Al₂O₃ (around 300 cm²/g) and with the mesoporous material “*par excellence*”, that is SiO₂ (typically around 1000 cm²/g). This is probably the reason why many reports are found about the use of mesoporous silica (mainly SBA-15) as support or additive for Ni-based catalysts [65, 87, 88]. In particular, in some of these reports the intrinsic properties of the porous (inert) support are coupled to that of the CeZrO₂ one [87, 88]. A positive effect towards sintering was reported, suggesting that the silica pores could prevent the aggregation of nickel [88].

3. Catalysts for low temperature steam reforming

2.3. General concepts

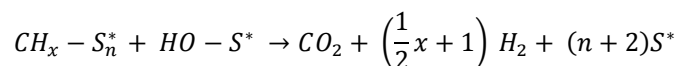
A comprehensive review about the most studied catalysts for low temperature MSR was recently reported by Angeli et al. [89]. The authors considered three major groups of materials: nickel-based, noble-metal based and bimetallic catalysts, concentrating on their catalytic performances and related kinetic models. When Ni-based catalysts are reviewed, a large variety of oxide supports were compared. Among these, CeO₂ or CeZrO₂ based catalysts showed interesting performances [70]. Noticeably, these same supports were widely employed for low temperature SR catalysts based on Rh, Ru, Pt or Pd, while “classical” supports (mainly γ -Al₂O₃ and MgAl₂O₄) were explored for bimetallic active phases [70].

The point of view of this contribution is not focused on the catalytic performance itself, but on the structural and surface properties of active phases and supports, with particular attention to the influence on the catalysts activity and stability. Some of these properties were already mentioned and discussed in the previous paragraphs, since the issues are similar when dealing with high or low temperature processes. In both cases the percentage of hydrogen in the product mixture is governed by thermodynamics, but the catalyst can affect methane conversion and obviously influence the reaction kinetics, with its turnover frequency (TOF), diffusion issues etc. [89]. The other important aspect is catalyst stability, especially when Ni-based catalysts are employed. Even if both nickel sintering and carbon deposition are usually explained with the harsh conditions of the industrial process, both phenomena can take place at relatively low temperature, and the choice of the support can be fundamental to avoid or limit these problems [79, 85, 90].

2.2. Structure, active sites and mechanisms

With the above considerations in mind, this paragraph will be mainly focused on the surface and structural properties of Ni-based catalysts, especially when CeO₂, or CeZrO₂ supports are employed. This choice is based on interesting properties of this support, largely investigated also in the low temperature SR reaction with noble metals [47][70].

Among the other employed supports, the interesting paper from Matsumura et al. [33] reported the comparison among Ni (20 wt%) supported on SiO₂, γ -Al₂O₃ and ZrO₂. The reaction was carried out at 773 K, with S/C = 2. The silica based catalysts was shown to deactivate quickly, while the employ of ZrO₂ as support showed the highest activity and stability, also at 5% Ni wt. The authors interpreted the results in terms of the supports surface properties, by feeding separately methane and carbon to the catalysts. Their interpretation was in terms of the formation of hydroxyl groups on the surface of zirconia as a consequence of water accumulation. The *in situ* formed mildly acidic hydroxyl groups were proposed to play an important role in low temperature methane conversion to H₂, following the reaction:



where S* are the surface active site, CH_x is supposed to be formed by adsorption on a partially reduced surface and HO-S* are the hydroxyl groups formed upon water accumulation [33].

As mentioned above, apart from this interesting report, most studies proposing correlations between structural/surface properties and performances are based on CeO₂, or CeZrO₂ supports. CeO₂ is an active support, widely employed in catalysis thanks to the reported enhancement of metal dispersion and SMSI [43, 69, 91-93]. Moreover, CeO₂ has a high “oxygen storage capability” (OSC), related to the presence of oxygen vacancies in defective sites that can be quickly formed and destroyed [94-96]. This feature could be useful to avoid deactivation as a consequence of coke formation. At high reaction temperature, however CeO₂ is readily sintered, which results in catalyst deactivation. It has been reported that the addition of ZrO₂ leads to improvement in thermal resistance and OCS of CeO₂ [97-101]. This was found to be due to the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the lattice of CeO₂, which results in a solid solution formation [102-104].

Ni/CeO₂ and Ni/CeZrO₂ catalysts, often prepared by quite simple co-precipitation reaction procedures, were reported to be active and stable in the low temperature SR process [35, 53, 88, 93, 105]. The reasons for this performances could be related to the support potential for SMSI with Ni particles and to the well known oxygen storage and exchange properties, favoring reaction of surface carbon deposits with mobile surface or lattice oxygen [53, 92, 93, 106, 107]. The intrinsic properties of ceria were further enhanced by the formation of thermally stable solid solutions with zirconia, resulting in easier reduction of ceria, as shown by temperature programmed reduction (TPR) experiments and high catalysts stability even at S/C = 1 [106].

Roh et al. [108] proposed that the enhanced catalytic activity and stability of the co-precipitated Ni/CeZrO₂ catalys (0.8 Ce and 0.2 Zr in atomic ratio) is related to the combination of the nano-crystalline nature of cubic Ce_{0.8}Zr_{0.2}O₂ support and finely dispersed nano-sized NiO_x crystallites. This would result in intimate contact between Ni and support, better Ni dispersion, higher Ni surface area and enhanced oxygen transfer during the reaction. This interpretation was mainly based on the correlation between catalytic results and powder X ray diffraction (XRD) results. Xu and Wang [107], pointed out that higher surface area and small particle size of Ni could be obtained by one-pot co-precipitation method, with respect to impregnation. This also favored a strong interaction of Ni with the support, in turns suppressing carbon deposition. This was also shown in Ref. [73], suggesting the incorporation of NiO in the surface of CeZrO₂, with consequent modifications of the chemical environment of nickel particles. The resulting lower reducibility of NiO could be exploited in providing oxygen atoms for carbon removal, thus enhancing the catalyst activity and stability [73].

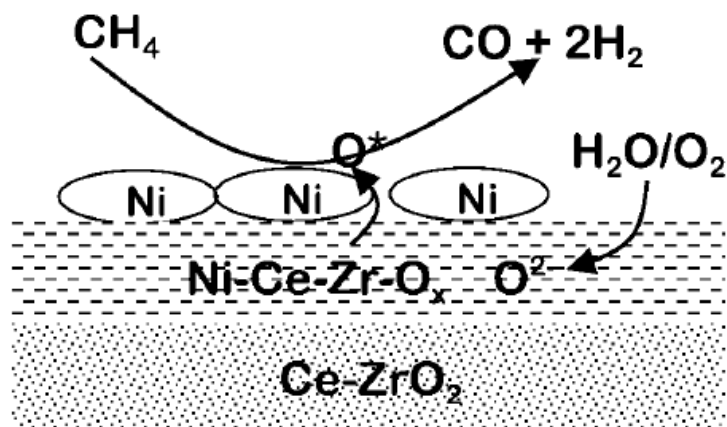


Fig. 10 Pictorial representation of the surface layers of Ni/CeZrO₂ catalyst, and proposed mechanism for syngas production. Reproduced from Ref. [106] with kind permission from Springer Science and Business Media.

Many schemes were proposed to explain the unusual properties of Ni/CeO₂ and Ni/CeZrO₂ catalysts. This is easily understood since the structural and surface properties of the active phase, support and interface can be characterized by many complementary techniques. As already mentioned, TPR is typically employed to study the reducibility of both Ni particles and support. These information could be combined with those obtained by X-ray photoelectron spectroscopy (XPS), which could provide details about the oxidation state and local environment of all surface atoms (Ni, Ce, Zr and O). This kind of analysis was carried out by Roh et al. [106], who also measured the amount of mobile oxygen in both supports and catalysts by pulse experiments. On this basis, the structure of catalysts surface could be proposed, as depicted in Fig. 10. The authors describe the catalyst as a composite of different layers. The top layer is composed by relatively free Ni particles, while an intermediate one with strongly interacting Ni and CeZrO₂ is sandwiched between top Ni and CeZrO₂ support. The same authors pointed out the higher loading of mobile oxygen in CeZrO₂ and CeO₂ with respect to ZrO₂, thus supporting the hypothesis that the OSC of ceria is at the basis of the peculiar properties of the catalyst [106].

In another contribution, Kumar et al. [53] showed the importance of zirconia in stabilizing and optimizing ceria properties by solid solution formation. In fact, Ni particles supported on ZrO₂ and Ce-doped ZrO₂ catalyst were found to be less stable in low temperature methane dry reforming with respect to Ni on a CeZrO₂ solid solution. In this case the stability towards carbon deposition was studied by temperature programmed oxidation (TPO) experiments, coupled to TPR [53]. Another interesting report was instead focused on a new Ni₁₀Ce₉₀ mixed oxide, which coupled the usual claims about high stability towards coke formation and high activity to the unusual observation of an immediate activity without pre-activation (usually carried out to obtain Ni metal particles) [53]. This was explained by the important role of interfacial oxygen and by a balance between the rate of generation and supplement of oxygen vacancies.

Another unusual observation about Ni/NiO redox properties on CeZrO₂ was reported by Gopalakrishnan et al. [90]. The authors studied a Ni/CeZrO₂ catalyst prepared by co-precipitation in the low temperature methane SR, and tried to correlate its high stability (up to 250 hours with S/C = 2 or 3) to structural and surface properties. The sample was characterized by well defined crystalline CeZrO₂ particles (5-6 nm average size) with spherical/hexagonal morphology (Fig. 11). Nickel particles could not be directly observed by TEM, due to the low contrast between Ni and the support atoms, but Fourier Transform analysis confirmed the presence of small NiO particles (5 nm as average size) in intimate contact with the support, as suggested by Roh et al. [108]. Interestingly, when the sample was reduced in hydrogen and then exposed to atmosphere, a rapid change in color from black to dark brown was observed, suggesting the transformation from Ni⁰ to NiO, as confirmed by both XRD and TEM measurements. This extreme reactivity of supported Ni⁰ particles was related to the strong interaction with the support, displaying oxygen vacancies on the surface, as schematically represented in Fig. 12. Interestingly, a NiCeZrO₂ prepared at different pH did not show this phenomenon. This catalyst was characterized by larger Ni particles (10 nm) and showed deactivation due to carbon deposit formation and sintering [90].

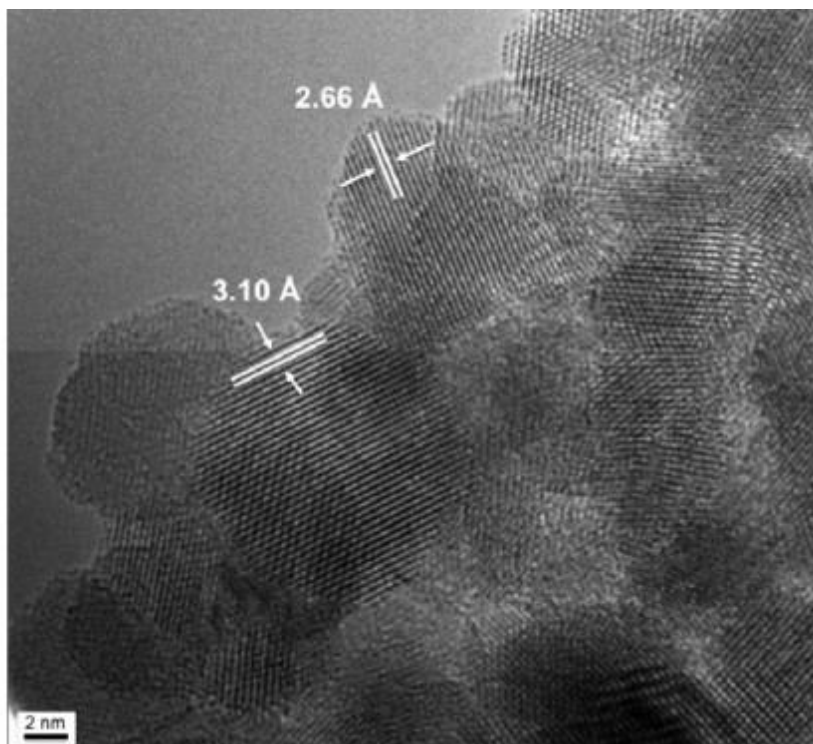


Fig. 11 TEM image of a NiCeZrO_2 catalyst prepared by co-precipitation. The particles are characterized by lattice distances compatible with a cubic CeZrO_2 phase. Adapted from Ref. [90] with permission from Elsevier.

Other models and mechanisms were proposed by several authors to explain the intriguing properties of metal or oxidic particles supported on CeO_2 based catalysts, by employing many characterization techniques. It is not possible in this context to review all the impressive literature on the subject. A mention is however made to the very interesting works reported by Caballero et al. [69, 70]. The authors studied Ni/CeO_2 systems by *in situ* X-ray absorption spectroscopy (XAS) and X-ray photoemission experiments under near-ambient pressure conditions (APPEs). These techniques allowed following changes in morphology of Ni particles during reduction or SR reactions. More in detail, the burial and digging out of metallic nickel on the surface of ceria was monitored, as a consequence of SMSI and ceria moieties migration (Fig. 13) [69]. Finally, it is important to mention the fact that similar models and reaction mechanisms were proposed in the literature to explain the activity of noble metal supported on CeO_2 or CeZrO_2 for low temperature SR processes [47].

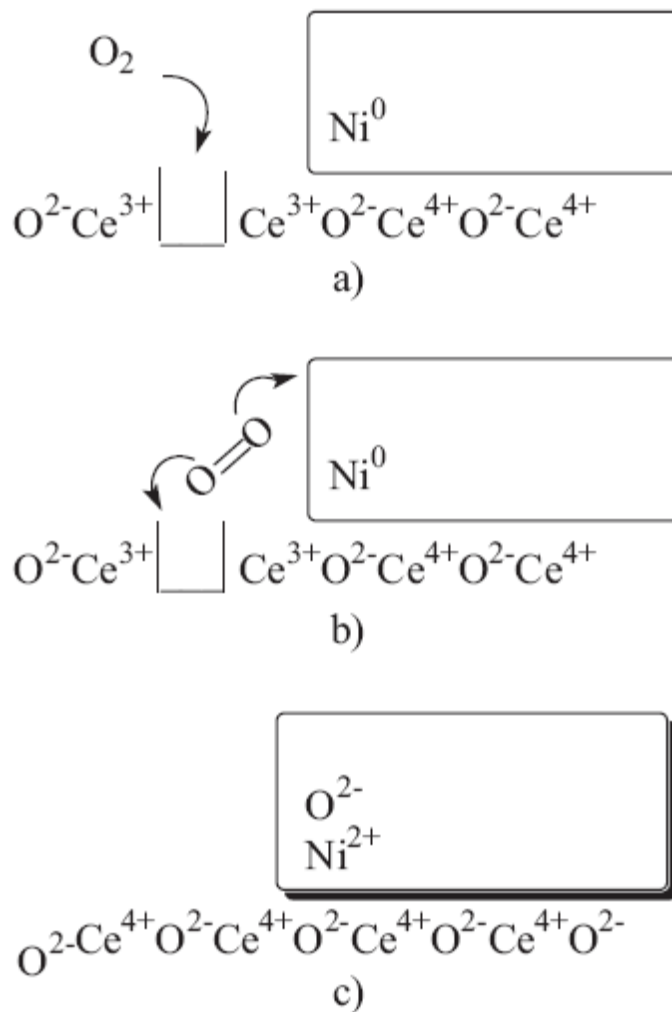


Fig. 12 Simplified representation of room temperature oxidation of a previously reduced Ni-CeZrO₂ surface as a result of contact with atmospheric oxygen. Reprinted from Ref. [90] with permission from Elsevier.

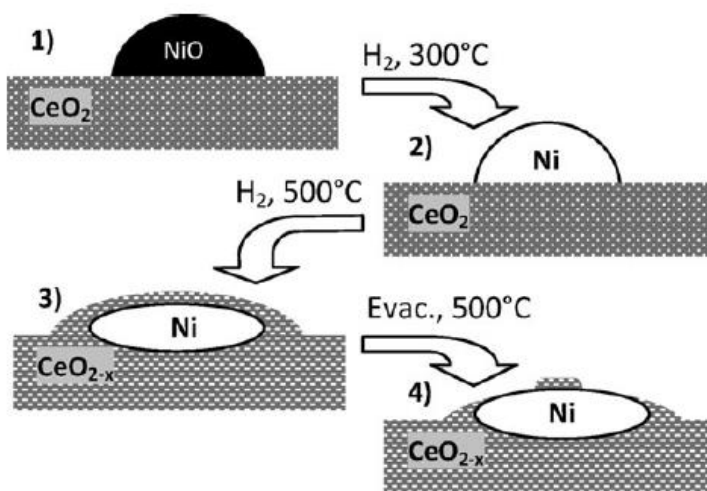


Fig. 13 Schematic evolution of Ni/CeO₂ system submitted to reduction and evacuation treatments. Reproduced from Ref. [69] with permission of The Royal Society of Chemistry.

Conclusions

This contribution deals with the surface and structural properties of catalysts for low temperature MSR. The importance of this reaction from the energetic and environmental point of view was discussed, by considering the direct synthesis of EM as a shortcut towards the “hydrogen economy”. Then, the general requirements and issues of catalysts for SR were described, with particular attention to the improvements obtained by promoters and a careful selection of the support. This discussion suggested that one of the main points for the development of low temperature SR catalysts is not the selection of the active phase (both Ni and noble metal particles are highly active in a large range of temperature) but of the support. The interaction of the active phase with the support is in fact essential to increase its dispersion, surface area and to stabilize metal particles towards sintering during SR reaction. Hence, stability of the catalysts towards deactivation is crucial for the low temperature reaction as in classical process. This includes the ability of promoters, supports or metal/support interfaces in suppressing carbon deposition mechanisms.

In this context, the attention is focused on Ni/CeO₂ or NiCeZrO₂ catalysts, since this class of materials (especially when prepared by one-pot co-precipitation) has shown interesting low temperature activity and many surface and structural studies were reported to explain their properties and catalytic behavior. This complex surface chemistry could be useful also to interpret the activity in the same reaction of noble metal catalysts (mainly Ru and Rh). Two main mechanisms are proposed for the low temperature SR activity and stability from the point of view of surface sites structure. One is based on the role of surface hydroxyl on ZrO₂ supports, while the other, investigated in deeper detail, focuses on the oxygen storage and exchange properties of ceria, stabilized by the formation of solid solutions with zirconia. The intimate contact of Ni (or noble metal) particles with the CeO₂/CeZrO₂ support, through SMSI and oxygen/vacancies exchange equilibria, are the basis to interpret the high activity at low temperature coupled to stability towards sintering and carbon growth.

List of acronyms

APPES	Ambient pressure photoemission spectroscopy
CSP	Concentrating solar plant
CCS	Carbon capture and sequestration
EM	Enriched methane
FC	Fuel cells
ICE	Internal combustion engines
LNG	Liquefied natural gas
MS	Molten salt
MSR	Methane steam reforming
NG	Natural gas
OSC	Oxygen storage capability
SMSI	Strong metal-support interaction
SR	Steam reforming
TEM	Transmission electron microscopy
TOF	Turnover frequency
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
WGS	Water gas shift
XRD	X ray diffraction
XPS	X-ray photoelectron spectroscopy
XAS	X-ray absorption spectroscopy

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