

# Dry and steam reforming of methane. Comparison and analysis of recently investigated catalytic materials. A short review.

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In order to produce valuable syngas, industrial processes of dry reforming of methane and steam reforming of methane must be further developed. This paper is focused on reviewing recently examined catalysts, supporting the mentioned technologies. In both processes the most popular active material choice is usually nickel, due to its good availability. On the other hand, noble metals, such as ruthenium, rhodium or platinum, provide better performance, however the solution is not cost-effective. Materials used as a support influence the catalytic activity. Oxides with basic properties, such as MgO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, are frequently used as carriers. One of the most promising materials for reforming of methane technologies are hydrotalcites, due to adjustable composition, acid-base properties and possibility of incorporation of various metals and complexes.

**Keywords:** dry methane reforming, steam methane reforming, nickel catalyst, hydrotalcite.

## INTRODUCTION

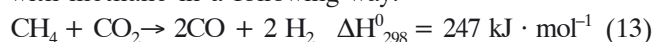
Nowadays, when the negative results of an industrial development are more visible as environmental changes such as depletion of ozone layer, greenhouse effect and acid rains, substitution of fossil fuels by clean energy sources will be one of the solutions leading to a sustainable energy development. Especially interesting is hydrogen, which could be used as a fuel for the fuel cells, be traditionally combusted with release of environmentally neutral water, or supplied for the production of synthetic fuels which are free from sulphuric ingredients<sup>1</sup>.

Widely used method for a hydrogen production is steam reforming of methane. The volume of hydrogen and efficiency of the process are much more satisfactory than in other methods, for example water splitting through electrolysis which require big energy input<sup>2</sup>. Dry reforming of methane is considered as a way of energy storage through the closed loop thermochemical heat pump<sup>4</sup>. Also, the product of the dry reforming of methane is syngas with carbon monoxide to hydrogen ratio of 1, which makes it a perfect feedstock for Fischer-Tropsch synthesis<sup>5</sup> which in turn depends on the product selectivity. The kinetics, reactor requirements, control of selectivity and the life of cobalt and iron catalysts are discussed and compared. Control of the FT conditions coupled with appropriate downstream processes results in high yields of gasoline, excellent quality diesel fuel or high value linear  $\alpha$ -olefins. The history of the various FT options and of the improvements in FT reactor technologies over the last 50 years is reviewed. It appears that “new” technologies are re-discovered in cycles of 15–30 years and it often takes the same time for the implementation of new concepts. Similar type of syngas may be produced via partial oxidation of methane, which is a process competitive to dry reforming, based on a reaction between below-stoichiometric volume of oxygen and methane<sup>6</sup> based on experimental power rate law equations described in a previous paper and classical kinetics. According to Boudart’s school approach of Classical Kinetics, kinetic rate equations of TOM and DRM reactions were then established based on the Quasi-Steady State Approximation (QSSA).

There are a few paths for reforming methane, depending on the initial gas mixture and reforming medium. The methane oxidizing agent may be carbon dioxide, steam or oxygen, according to a provided technique<sup>10</sup>. Catalytic reforming processes are likewise an efficient way for utilization of biogases such as landfill gas, which do not have a production rate constant in time, thus cannot be used as a fuel for a continuous combustion. However, their main ingredient, methane, has a well-known reforming potential<sup>11</sup>.

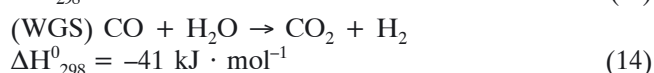
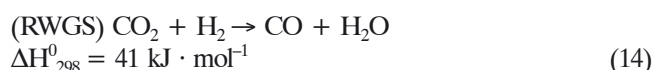
## Dry reforming of methane (DRM)

Dry reforming of methane is technologically simpler than steam reforming, due to the lack of water evaporation, but with the lower hydrogen production yield<sup>12</sup>. The idea behind this process is to react carbon dioxide with methane in a following way:

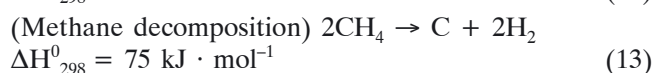
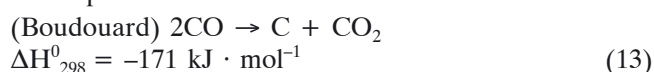


As shown in equation above, methane is a reducing agent and carbon dioxide is an oxidant. This type of reaction may be applied to gases with both CO<sub>2</sub> and CH<sub>4</sub> content, such as biogases. It is also a method for CO<sub>2</sub> mitigation.

There are several side-reactions accompanying DRM process, among them reverse water-gas shift reaction (RWGS) and water-gas shift reaction (WGS), the result of operation conditions, in which water can be generated.



Other inconvenient reactions, especially from the point of view of an applied catalyst, are carbon deposits formation<sup>15</sup> via the Boudouard reaction or methane decomposition<sup>16</sup>.

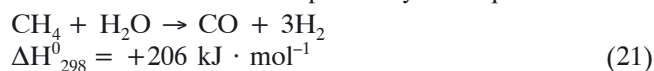


The main reforming reaction is highly endothermic, and the whole process requires energy supply and high temperature. At the same time, according to the Le

Chatelier's principle, the pressure of the process should be low. *Temperatures usually applied are in the range of 500–1000°C with pressure of 1–20 atm*<sup>17</sup>. 1000°C is a temperature limit because of nickel carbide formation on the catalyst surface. On the other hand, in temperature above 600°C the formation of pyrolytic coke over the active surface sites is decreasing the overall activity due to deactivation of the nickel sites<sup>18</sup>. The reactor feed is usually the stoichiometric ratio of carbon dioxide and methane, which results in such conversion that no CO<sub>2</sub> recovery is required. It is possible to reach conversion of even 98–99% with the proper temperature-pressure balance. The higher the temperature and lower the pressure, the process efficiency is closer to 100%<sup>19</sup>, but at the same time it requires high energy input and an advanced installation which results in high cost<sup>20</sup>

### Steam reforming of methane (SMR)

The idea behind the steam reforming process is to convert hydrocarbons into a mixture of hydrogen, carbon monoxide, carbon dioxide and methane. It is currently the main industrial process of H<sub>2</sub> production. The main SMR reaction can be simplified by the equation below.



A reverse reaction to above equation is also possible and shown below.



### The reaction is performed on a nickel catalyst.

SMR reaction is highly endothermic. Water-gas shift reaction and methanation reaction are exothermic and reversible at reforming temperature. *Steam reforming process is carried out at high temperature range, usually 700–1100°C.*

During the steam reforming of methane (SMR) process, the same carbon forming side-reactions are possible as in the dry reforming process, Boudouard reaction and methane decomposition are reversible at the temperature of the process.

The composition of the produced syngas can be estimated basing on thermodynamic calculations. The H<sub>2</sub>/CO ratio in the final gas mixture is influenced by process parameters such as steam pressure and temperature. *Usually pressure inside the reactor is in the range of 3–25 atm, depending on the technology used*<sup>23</sup>. The lower the pressure the higher the process efficiency according to the Le Chatelier's principle. Volume balance of products and reagents are important for high conversion – high values of applied temperature and steam-to-carbon ratio are required as steam is oxidizing the coke to carbon oxides, protecting the catalyst from rapid deactivation<sup>21</sup>. *On the other hand, modern hydrogen plants are designed to operate with the low steam to carbon ratio of 1.8–2.5 mol steam/ mole CH<sub>4</sub> which is beneficial from the point of view of mass flow through the plant, size and costs of the equipment, lower operating costs and higher energy efficiency*<sup>24</sup>.

### Catalysts for methane reforming processes

A proper choice of catalytic material influences efficiency of the operation. Both active material and support

are important. Different support materials have been investigated, but still the most popular is  $\gamma\text{-Al}_2\text{O}_3$ <sup>25</sup>. *The catalyst may have different structure, from powder, grained catalyst to structured forms, such as monolith, honeycomb or open cell foams.* The most popular active material is nickel in high concentration. It may be promoted with noble metals such as e.g. platinum. Typical problems for reforming catalysts are sintering and coking.

### Dry reforming of methane

Catalysts for DRM suffer from deactivation caused by catalytic coke. The process is influenced by temperature. Higher rate of coking is promoted by lower temperatures, below 700°C, where the Boudouard reaction reaches higher rate. Noble metal catalysts showed high activity and good stability against coking. On the other hand, nickel catalysts, showed high activity in DMR process, but they were not resistant against coking<sup>26,27</sup>. Their stability can be improved by preserving small Ni nanoparticles with strong metal-support interactions<sup>28</sup> total pressures of 0.1 and 0.5 MPa and a CO<sub>2</sub>/CH<sub>4</sub> ratio of 1. The kinetic data including carbon formation and deactivation were measured simultaneously by an oscillating microbalance reactor. A microkinetic model was developed to analyze the kinetic data and extended with reactions for the carbon formation (encapsulating and filamentous. This may be achieved on a proper support. NiMgO systems were also investigated, but it is hard to reduce Ni<sup>2+</sup> in NiO-MgO solid solution<sup>16</sup>.

Noble metal catalysts such as Ir or Ru supported on Al<sub>2</sub>O<sub>3</sub> usually exhibited high activity and selectivity for reforming of methane. Ni catalyst was initially active but demonstrated worse selectivity and became deactivated rapidly due to coking. Adding small amounts of steam to the feed improved stability of a catalyst and decreased deactivation rate<sup>29</sup>.

The comparison of selected catalysts and their performance in dry reforming was given in Table 1.

Osazuwa et al.<sup>30</sup> found that the improvement of catalytic performance was possible without the addition of noble metals. Activity and stability were increased by using transition metal catalyst with the perovskite support. The combination of the rare earth metals, transition metals and oxygen in perovskite structure resulted in high catalyst activity and stability. Perovskites have another advantage – high thermal stability. They may also be easily modified by substitution of different cations.

The properties of Ni and Ru catalysts supported on Al<sub>2</sub>O<sub>3</sub> on AISI 316 foam were also tested for the dry reforming process. AISI 316 foam exhibited long-term stability and high catalytic activity. Coating AISI 316 foam with Al<sub>2</sub>O<sub>3</sub> led to an increase in reactivity. AISI 316 was a foam Fe-based alloy, containing additional elements such as 18% of Cr, 10% Ni and 3% Mo. Ruthenium containing catalyst was reported to exhibit higher activity than the nickel containing one (Table 1). Erdogan et al.<sup>31</sup> related that although high temperature of 600–1000°C and reactant atmosphere may cause some changes in composition of AISI 316 foam matrix, long-term stability remained unaffected.

Natural illite clay enriched in magnesium and applied on a honeycomb monolith was also used as a base for nickel catalyst. The incorporation of nickel and magne-

**Table 1.** Comparison of catalyst for dry reforming of methane

Active Material	Support	Conditions	CO <sub>2</sub> Conversion [%]	References
Ru (0.5% wt.)	Al <sub>2</sub> O <sub>3</sub>	p = 1 atm, T = 850°C, ratio CH <sub>4</sub> :CO <sub>2</sub> = 1.3:1	99	19
Rh (5% wt.)			98	
Ir (1% wt.)			96	
Pt (0.5% wt.)			98	
NiO (25–45% wt.)			Al <sub>2</sub> O <sub>3</sub> (45–65% wt.) – Ca aluminate (3–8% wt.)	
Ni (55–60% wt.)	kieselguhr		93	
SmCoO <sub>3</sub>	perovskite	p = 1 atm, T = 800°C, ratio CH <sub>4</sub> :CO <sub>2</sub> = 1:1	93	20
Ru (2% wt.)	Al <sub>2</sub> O <sub>3</sub> /AISI 316 foam	p = 1 atm, T = 900°C, ratio CH <sub>4</sub> :CO <sub>2</sub> = 1:1	<b>CH<sub>4</sub> conversion [%]</b> >90	21
Ni (5% wt.)	Al <sub>2</sub> O <sub>3</sub> /AISI 316 foam	p = 1 atm, T = 1000°C, ratio CH <sub>4</sub> :CO <sub>2</sub> = 1:1	~89	
Ni (8% wt.) Mg (3%wt.)	natural illite clay on monolith	p = 1 atm, T = 1000°C, ratio CH <sub>4</sub> :CO <sub>2</sub> :O <sub>2</sub> = 5:4:1	89	22
Ni (14% wt.)	S-1 coated SiC support	p = 0.987 atm, T = 750°C, ratio CH <sub>4</sub> :CO <sub>2</sub> :O <sub>2</sub> = 8:2:3	66	23
K (0.4% wt.), Ni (5.3% wt.), Ca (11.7% wt.)	ZSM-5	p = 1 atm, T = 800°C, ratio CH <sub>4</sub> :CO <sub>2</sub> :N <sub>2</sub> = 1:1:2.2	>90	24
Ni:Co in ratio 1:2			>85	
Ni:Co in ratio 1:1			>80	
Co			<80	
Ni	hydrotalcite	p = 1 atm T = 550°C, ratio CH <sub>4</sub> :CO <sub>2</sub> :Ar = 1:1:8	53	26
Ni-Ce	hydrotalcite		54.8	
Ni – Zr	hydrotalcite		25	
Ni (19% wt.)	nanocapsular hydrotalcites	p = 1 atm T = 800°C	94	28
Ni	CeZr 950	p = 1 atm, T = 750°C, ratio CH <sub>4</sub> :CO <sub>2</sub> = 0.66:1	~44	6
	CeZrNd <sub>0.2</sub> 990		~57	
	CeZrNd <sub>0.07</sub> 1030		~58	
Ni 10%	La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>	p = 1 atm, T = 700°C, ratio CH <sub>4</sub> :CO <sub>2</sub> = 1:1	<90	5
Ni	SiC foam monolith with CNF's	p = 0,987 atm, T = 750°C, ratio CH <sub>4</sub> :CO <sub>2</sub> :Ar = 45:45:10	75	29

sium into the clay increased significantly the density of basic sites. This also results in the increased resistance to coking. Some elements present in clay, e.g. potassium, can promote carbon dioxide activation in NiO-MgO solid solution, providing adsorbed oxygen species and carbon monoxide. This type of catalyst was found to have satisfactory stability for 24 hours<sup>32</sup>.

Interesting research was also carried out using zeolites, e.g. silicalite-1 zeolite which was resistant to high temperatures and remained in its crystalline form. It was used as a coating, playing the role of an intermediate between active material and SiC support. Acidic supports such as zeolites were prone to coke deposition which led to a decrease of activity and shortens their lifetime. S-1, unlike other zeolites, does not have high acidity and was thus more resistant against coking during methane dry reforming than other zeolite materials from this group<sup>33</sup>.

ZSM-5 has also been investigated as a support for DRM. Ni deposited on ZSM-5 was reported to have both good activity and resistance towards coke deposition for 140 hours<sup>34</sup>. Estephane et al.<sup>35</sup> tested Co and Ni-Co deposited on the ZSM-5. The bimetallic catalyst with cobalt content two times higher than that of nickel gave the best results (Table 1), with the highest activity, stability and low carbon deposits formation after 12 hours.

It was assigned to cobalt playing the role of an oxidizing agent for the removal of carbon species.

Other type of materials studied as catalysts for DRM were hydrotalcites. Both acidic and basic sites may be found on hydrotalcite surface. Gonzalez et. al<sup>36</sup> studied nickel-hydrotalcites. The best results were obtained for the highest tested loading of nickel of 19 wt.%. Both activity and selectivity were high, with minimal coke deposition under the optimized conditions of 650°C. Dębek et. al<sup>37</sup> carried out an extensive research on DRM on hydrotalcites. Several types of hydrotalcites were tested, with different content of Mg<sup>2+</sup> ions substituted with Ni<sup>2+</sup>. Moreover, the addition of promoters such as cerium and zirconium was studied. The latter increased the reducibility of nickel species and improved dissociative adsorption of CO<sub>2</sub> on the catalyst sites. It should be also mentioned that catalysts were efficient at a relatively low DRM temperature range. Especially Zr presence impacted strongly both activity and selectivity of the catalyst<sup>38, 39</sup> resulting in materials with various Zr loading. Physicochemical properties of catalysts precursors and final catalysts were investigated via XRF, XRD, low temperature N<sub>2</sub> sorption, H<sub>2</sub>-TPR, CO<sub>2</sub>-TPD, TG, SEM and TEM techniques. So characterized catalysts were subsequently tested in the dry methane reforming

reaction at 550°C. Zr-loading introduced into brucite-like layers influenced the process of thermal decomposition of HTs and, as a result, their properties and performance in DRM. Although Zr promotion decreased activity, it strongly increased the stability and selectivity of the catalysts. The catalyst with Zr species present in the framework of periclase-like mixed oxide exhibited high resistance to coking due to the rearrangement of Ni particles upon DRM reaction.

La-promoted Ni-hydroxalcalite derived catalysts were investigated in a DRM process at low temperatures (550°C) by Liu et al.<sup>41</sup>. Lanthanum incorporation to the catalyst resulted in enhancing the reforming reaction and direct methane decomposition at given temperature conditions. Also, La supports carbon deposits gasification, which results in lower amount of coke on a surface of the catalyst. Obtained methane conversion during the catalytic test reached 33% for the  $\text{Ni}_{0.215}\text{La}_{0.012}\text{Mg}_{0.535}\text{Al}_{0.238}$  sample at range 550–600°C, and at 850°C the same catalyst showed almost full conversion of methane.

Pappacena et al.<sup>14</sup> prepared a set of zirconium and neodymium doped catalysts via a surfactant assisted co-precipitation method. The samples varied in the amount of introduced Nd and Zr. As the catalytic tests showed, the conversion of methane at 750°C did not exceed 60%, but CO<sub>2</sub> conversion in given conditions was over 90%. What is important, the dopants do influence the kinetics of the process, especially inhibiting the reverse water-gas shift reaction. Nd and Zr addition made it possible to control basicity and surface oxygen mobility while increasing the resistivity of the catalyst against coke formation.

Stabilizing the active material inside the thermally stable structure of oxide such as pyrochlores should lead to the increase in oxygen mobility over the surface and decrease in sintering, though the accessibility of such an active site, locked inside the highly stable structure, may be questionable. Le Sach'e et al.<sup>13</sup> provided the research on Ni-doped  $\text{La}_2\text{Zr}_2\text{O}_7$ . The obtained material varied strongly during the stability test – when the catalyst with 5% Ni lasted only for 30 hours on stream, the one with 10% Ni was resistant for 360 hours. Likewise, the catalytic performance in DRM process for 10% Ni catalyst was satisfactory, despite the carbon nanotubes formation on the surface.

Gao et al.<sup>42</sup> focused on a research for a catalyst stable in a DRM process. Ni as the active material was deposited on the SiC foam monolith covered with carbon nanofibers. The addition of nanomaterials increased strongly the specific surface area. Such kind of the support provided both high dispersion and strong attachment of the active sites to the surface, which resulted in a catalyst that was resistant for 100 hours on stream.

### Steam reforming of methane

At industrial furnace for methane steam reforming, the reactor inlet temperature is in the range of 450–650°C and at the outlet region temperature grows to 850–950°C<sup>43</sup>. Thus, a catalyst must be resistant towards sintering, and a chosen support must be temperature-stable and resistant to phase changes<sup>44</sup>.

The comparison of selected catalysts and their performance in steam reforming is given in Table 2.

Catalysts containing nickel as an active material have been the first choice of studies in the methane steam

**Table 2.** Comparison of selected catalyst for steam reforming of methane

Support	Active Material	Conditions	Methane conversion [%]	References
Al <sub>2</sub> O <sub>3</sub>	Ni (9.8% wt.) S (4.9% wt.)	p = 1atm, T = 700°C, H <sub>2</sub> O:CH <sub>4</sub> : air = 2.5:1:3.5	99	33
Al <sub>2</sub> O <sub>3</sub>	Ni (7% wt.) Mg Al	p = 0.987atm, T = 600°C, H <sub>2</sub> O:CH <sub>4</sub> = 2:1	>80	34
Al <sub>2</sub> O <sub>3</sub>	Ni (8.6% wt.) Zn Al	p = 0.987atm, T = 600°C, H <sub>2</sub> O:CH <sub>4</sub> = 2:1	>75	
SiO <sub>2</sub>	10(% wt.) nano-NiO	p = 1atm, T = 700°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	95.7	35
SiO <sub>2</sub>	Ni (10%wt.)	p = 1atm, T = 700°C, H <sub>2</sub> O:CH <sub>4</sub> = 2:1	>35	36
CeO <sub>2</sub>	Rh (1.5% wt.)	p = 1atm, T = 635°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	>99	37
Al <sub>2</sub> O <sub>3</sub>	Rh (1.5% wt.)	p = 1atm, T = 660°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	>99	
CeO <sub>2</sub>	Ru (1.5% wt.)	p = 1atm, T = 699°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	96.8	
Al <sub>2</sub> O <sub>3</sub>	Ru (1.5% wt.)	p = 1atm, T = 699°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	>99	
CeO <sub>2</sub>	Pt (1.1% wt.)	p = 1atm, T = 800°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	<80	
Al <sub>2</sub> O <sub>3</sub>	Pt (1.1% wt.)	p = 1atm, T = 745°C, H <sub>2</sub> O:CH <sub>4</sub> = 3.5:1	>99	
MgO	Ru	p = 1 atm, T = 750°C, H <sub>2</sub> O:CH <sub>4</sub> = 2.8:3	>98	38
Nb <sub>2</sub> O <sub>5</sub>	Ru	p = 1 atm, T = 700°C, H <sub>2</sub> O:CH <sub>4</sub> = 2.8:3	>99	
metal foam	Pd (1.15% wt.) – Rh (0.16% wt.)	p = 1 atm, T = 750°C, H <sub>2</sub> O:CH <sub>4</sub> = 2.5:1	96.7	39
spirally wound honeycombe	Ni foil	p = 1 atm, T = 800°C, H <sub>2</sub> O:CH <sub>4</sub> = 1.34:1	>97	40
La (3% wt.) – Al <sub>2</sub> O <sub>3</sub> (ceramic monolith 100cps)	Ru (1.5% wt.)	P = 1atm, T = 800°C H <sub>2</sub> O/C:3:1	>99	41
La (3% wt.) – Al <sub>2</sub> O <sub>3</sub> (ceramic monolith 170 cps)	Ru (1.5% wt.)		>99.5	
La	NCZO	p = 1 atm, T = 900°C, H <sub>2</sub> O:CH <sub>4</sub> :N <sub>2</sub> = 1:1:3	95	42
Ru (3%wt.)	ZnLaAlO <sub>4</sub>	p = 1 atm, T = 800°C, H <sub>2</sub> O:CH <sub>4</sub> :N <sub>2</sub> = 1:1:3	<99	43
Ni	50%Ce 50%Ti	p = 1 atm, T = 500°C, H <sub>2</sub> O:CH <sub>4</sub> :N <sub>2</sub> = 1:1	>60	44
BrNi <sub>1.6</sub>	ZrO <sub>2</sub> hollow shell	p = 1 atm, T=750°C, H <sub>2</sub> O:CH <sub>4</sub> = 2.5:1	<99	45

reforming process. Ni supported on  $\text{Al}_2\text{O}_3$  is a promising catalyst, due to its low price and significant activity<sup>45, 28</sup>. Catalytic activity of  $\text{Ni}/\text{Al}_2\text{O}_3$  was found to increase with nickel content because of the increasing number of sites. On the other hand, the more nickel sites the higher their aggregation. A typical nickel content in a catalyst for steam reforming was ca. 12 wt.% to avoid aggregation and decrease sintering during the process. Bej et al.<sup>46</sup> prepared a catalyst on the  $\text{SiO}_2$  support with nano-NiO as an active material. Highly dispersed nickel oxide was introduced by the sol-gel method. The obtained catalyst showed stable methane conversion for 3.5 hours. Zhang et al.<sup>47</sup> investigated likewise 10%  $\text{Ni}/\text{SiO}_2$  catalyst, however instead of calcination, it was treated with DBD plasma for 1 hour. The overall conversion of methane did not exceed 40% but stability test resulted in 7 hours on stream.

The promotion of an SMR catalyst with other metals may also have a positive impact on its performance. Nieva et al.<sup>48</sup> studied the addition of zinc and magnesium to nickel-alumina catalyst at low temperature steam reforming. Ni-Zn-Al catalyst showed higher activity than Ni-Mg-Al, with the lower ratio of coking. It was found, however, that zinc sublimated during steam reforming, and thus the catalyst had to be activated at 600°C. No Ni sintering was registered which was assigned to metal-support interactions preventing migration.

Nickel catalysts required usually higher active material loading as compared to noble metals, the latter being at the range of 1–2%. Amjad et al.<sup>49</sup> studied the application of Rh, Ru and Pt on different supports, such as  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$ , in the methane steam reforming process. The best performance, high activity at low temperature (ca. 600°C) and good selectivity to methane was found for 1.5%  $\text{Rh}/\text{CeO}_2$ . This catalyst generated hydrogen-rich gas with low concentration of carbon monoxide, which was crucial from the point of view of hydrogen production. Other materials also showed satisfactory performance. Ru deposited on the  $\text{Al}_2\text{O}_3$  reached full conversion at 699°C, Pt deposited on  $\text{CeO}_2$  at 745°C. As shown in Table 2, the worst result was obtained for Pt on  $\text{Al}_2\text{O}_3$ , which did not show methane conversion higher than 80%.

Ru-based catalysts were reported to have high activity and selectivity during the steam reforming of methane. They remained resistant towards coking and sintering even at high temperatures (800°C). Amjad et al.<sup>50</sup> studied Ru on different supports –  $\text{MgO}$  and  $\text{Nb}_2\text{O}_5$  were chosen.  $\text{MgO}$ -based catalyst had good activity in terms of  $\text{CH}_4$  conversion. Niobia provided strong bonding between the metal and the support.  $\text{Nb}_2\text{O}_5$  catalysts showed very good activity, most of them with full conversion in the range of 700–750°C.

Metal foam have been investigated lately as a useful material for steam reforming of methane. Due to an appropriate porous structure and possibility of preparation in a desired shape, with low heat capacity and high heat transfer, they reduced the formation of the hot spots inside the reactor. Another advantage of metal foam was that its application can reduce the pressure drop in a reactor and provide a better mixing of gases. Pd-Ru catalyst supported on a metal foam were studied by Roy et al.<sup>51</sup>. The investigated catalysts compared to the commercial ones, such as 13% wt.  $\text{Ni}/\text{Al}_2\text{O}_3$  and 8%  $\text{Ru}/\text{Al}_2\text{O}_3$ , showed better activity,  $\text{H}_2$  yield and competitive

stability. After 200 hours experiment, negligible traces of coke were found on the surface.

Catalysts in the form of nickel on honeycomb were also investigated. The catalyst was built of 30  $\mu\text{m}$ -thin nickel foil in the form of metallic honeycomb without the addition of either alumina or noble metals. The catalyst showed high conversion, as well as high hydrogen yield. Hardly were any carbon deposits detected on the surface. Ni oxidation led to gradual deactivation of the catalyst, but flowing hydrogen resulted in rapid regeneration. Temperature profiles confirmed good heat transfer between the catalyst and the surrounding gases<sup>52</sup>.

Ru supported on ceramic monoliths with a different number of channels per square inch, covered with  $\alpha$ -alumina coating modified with La was studied by Vita et al. Two catalysts, one with square and the second with hexagonal channels showed good performance during the process, reaching fast equilibrium methane conversion, with slightly better results for the monolith with higher cell density<sup>53</sup>.

$\text{Ni-Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  based materials with different dopants such as Mg, Ca, La and were examined. The best catalytic performance was obtained by the La-containing catalyst, due to very high Ni dispersion, strong interaction between active material and support. Moreover, La provides the strongest basicity from the investigated samples. According to Khani et al.<sup>54</sup> mixing ruthenium as an active material with lanthanum containing support led to superlative catalyst, providing not only excellent conversion but likewise good stability with 30 hours on stream, working with a conversion higher than 95% all that time.

Mixed oxides of cerium and titanium were prepared by the two different methods: sol-gel and flame spray pyrolysis, to compare their activity and stability in SMR process. The better results were obtained by catalysts prepared through sol-gel method, especially these containing more cerium than titanium. It was noted, that the samples prepared by sol-gel method were more stable during the stability tests<sup>55</sup>.

Lim et al.<sup>56</sup> investigated the influence of porosity on the catalytic performance in SMR process. The best results were obtained by the samples with medium values of  $S_{\text{BET}}$  from the compared ones, about 176–178  $\text{m}^2/\text{g}$ , and medium total pore volume, 0.48–0.52  $\text{cm}^3/\text{g}$ . This type of an active material was resistant during 48 hours on stream, resulting in very high conversion all this time.

On the other hand, it was found that in steam reforming zeolites should not be used, as they were thermally stable only up to 600°C, with water vapor damaging their structure over this temperature<sup>57, 58</sup>.

## CONCLUSIONS

Dry reforming of methane and steam reforming of methane could lead to the improvement of the quality of biogas and enable the utilization of landfill gas, in the latter case leading to added-value products. Research on active, stable and selective catalyst for both dry reforming of methane and steam reforming of methane is dominated by the nickel-containing materials, supported on basic oxides, very often modified. Doping with lanthanum, rhodium and ruthenium provides satisfactory activity

and stability, but it leads to increased costs of materials used. The catalysts for DRM and SMR can suffer deactivation due to active metal sintering and carbon deposition. The problem of sintering may be solved by preserving small metal particles over the catalyst surface by providing strong interaction with the support. Carbon deposition could be reduced through increasing the content of steam in a feedstock and optimizing temperature conditions of the process. In this respect, materials based on Ni-hydrotalcites are of special interest due to low costs of precursors, simplicity of preparation followed by the satisfactory activity and selectivity towards the reaction. High activity of such materials results from their basic properties, which may be tailored through appropriate composition. Their high stability towards sintering arises from strong interaction between active metal and support. High stability towards carbon deposits formation can be reached via appropriate promotion, e.g. with La or Zr. A lot of promising catalysts were investigated, but the most important aspect is optimization of costs of their production and exploitation. The accessibility of materials and repeatability of a catalyst production are of special importance, in order to apply a catalyst on industrial scale.

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