

Tri-reforming as a process of CO₂ utilization and a novel concept of energy storage in chemical products

Katarzyna Świrk^{1,*}, Teresa Grzybek¹, and Monika Motak¹

¹Department of Fuel Technology, AGH University of Science and Technology, Mickiewicza Av. 30, 30-059 Cracow, Poland

Abstract. Methane tri-reforming process is a combination of three reactions: steam methane reforming (SRM), dry methane reforming (DRM), and partial oxidation of methane (POM). The first two reactions have endothermic character, while the POM is the exothermic reaction, which allows to obtain the energy necessary for the other two processes in situ. CH₄ reacts with H₂O, CO₂, O₂, and synthesis gas is produced with desired H₂/CO ratios (1.5 – 2.0). The presence of H₂O and O₂ in the reaction environment can positively influence the stability of the used catalyst, by the inhibition of coke formation.

In this paper two scenarios for methane tri-reforming implementation are discussed: (i) Tri-reforming as a effective way for chemical CO₂ utilization, without the separation of carbon dioxide from flue gases from fossil fuel-fired power stations, and (ii) dry reforming of methane improved by the addition of water and oxygen, which may be applied as a chemical energy storage process. The literature on the subject of tri-reforming is shortly reviewed, including thermodynamics of the process, the possible conversions of methane and carbon dioxide, and proposed catalysts, both studied in tri-reforming, and in single processes (SRM, DRM and POM).

1 Introduction

Carbon dioxide is a gaseous compound which is also considered to be one of the main greenhouse effect causes. In 2014, among the total anthropogenic greenhouse gas (GHG) emissions, the two-thirds were represented by energy sector. In this share over 80% is assigned to the CO₂ presence. The early estimations performed by statistical office of the European Union (Eurostat) showed that CO₂ emissions had increased in 2015 compared with the previous year (change 2014/2015 was at level +0.7%) [1] in contrast to tendency which is observed from 2011 to 2014 with total decrease of CO₂ emissions to -9.6%,

* Corresponding author: swirk@agh.edu.pl

respectively at 2011/12 it was drop of -2.1%, at 2012/13 of -2.5%, and at 2013/14 it was observed CO₂ emission decrease of -5.0% [2-4].

The regulations which aim at declining concentration of greenhouse gases in the atmosphere were established [5]. Kyoto Protocol and European Union regulate the concentration of GHG emissions in the atmosphere (CO₂, CH₄, N₂O, HFCs, PFCs, SF₆) via long-time strategies (until 2050). In 2015, it took place the latest United Nations Conference on Climate Change (COP21, Paris) which assumes GHG reduction in order to preserve less than two-degree temperature growth above pre-industrial levels [5-7].

To facilitate decreasing and/or avoiding high CO₂ emissions related to energy production and use, the following methods are proposed: an increase in the efficiency of energy production, carbon capture and utilization processes (CCU), carbon capture and storage processes (CCS), and/or the application of renewable energy sources.

Particular attention is paid to CCU processes, where CO₂ can be used as feedstock in syntheses of desirable chemicals, as well as the CO₂ reputation may be improved by treating it as a valuable resource with almost zero costs of production [8]. Currently CO₂ is used in industry only on a limited scale. Urea synthesis is the best known process of CO₂ usage. The urea serves as a source of ammonia in order to reduce NO_x emission from the flue gases (in selective catalytic reduction process). The other known carbon dioxide syntheses are leading to the following products: salicylic (2-hydroxybenzoic) acid which is used as raw materials for the production of drugs; cyclic carbonates - used as solvents, and components of electrolytes in Li-batteries; polycarbonates from which are manufactured optical, automotive, and electronic components [9].

Another process which may utilize CO₂ is tri-reforming of methane (TRM), delivering synthesis gas (H₂/CO) in the presence of suitable catalyst.

In this paper two scenarios for methane tri-reforming implementation are shortly discussed: (i) TRM as a effective way for chemical CO₂ utilization, without the necessity of the separation of carbon dioxide from flue gases from fossil fuels fired power stations, and (ii) dry reforming of methane (DRM) improved by the addition of water and oxygen, which may applied as a chemical energy storage process.

2 Tri-reforming of methane

Tri-methane reforming is a combination of three main reactions which take place in the single reactor: steam methane reforming (SMR), dry methane reforming (DMR), and partial oxidation of methane (POM) [10]. The two first reactions have endothermic character, while the POM is the exothermic reaction, which allows to obtain the energy necessary for the other two processes in situ (see Fig. 1).

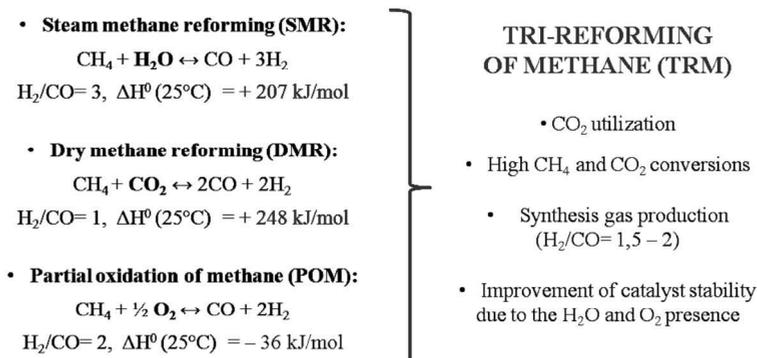


Fig. 1. Tri-reforming of methane with its main features

Thermodynamic tri-reforming calculations showed that high CH₄ and CO₂ conversions are possible. Song and Pan [10] reported respectively, over 95, and ca. 80 % at 800 – 850°C, under the following conditions: CO₂/H₂O molar ratio = 1.0, O₂/H₂O = 0.1, and the ratio of (CO₂+H₂O+O₂)/CH₄=1.05.

Moreover, the biggest advantage of the process is the production of synthesis gas which may be converted into methanol (MeOH) and liquid fuels (via Fischer-Tropsch synthesis). The syngas obtained in methane tri-reforming process has molar ratios in the range of 1.5 – 2.0 [10].

Additionally, the presence of H₂O and O₂ can positively influence the stability of the used catalyst, by the inhibition of catalytic coking [9,10], thus avoiding the stability problem common for dry reforming process, and improving lifetime of the catalyst. The formation and destruction of carbon deposits is the result of side reactions, depicted in Fig. 2: methane decomposition and Boudouard reaction leading to coke creation, and the latter reacting with CO₂, H₂O, and O₂.

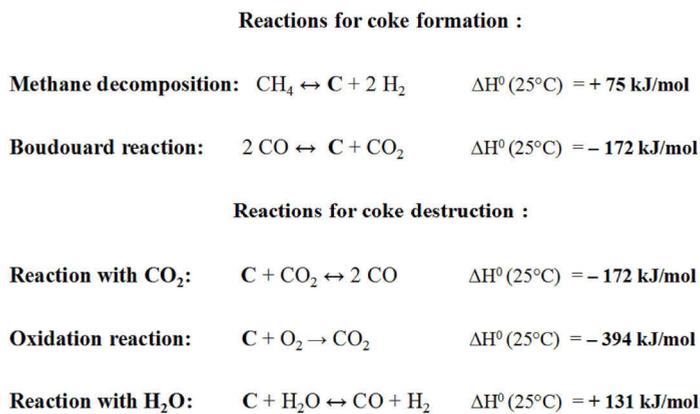


Fig. 2. Reactions of coke formation and destruction

2.1 Implementation of tri-reforming of methane

2.1.1 Chemical CO₂ utilization via TRM

CO₂ may be treated as a source of carbon for chemicals and fuels feedstock. Their production may be possible via tri-reforming of methane, which utilizes CO₂ in one of its reforming reaction.

The scenario applies to fossil fuel-fired power plants, where carbon dioxide is one of the components of flue gas. Fig. 3 shows the visualization of the concept where flue gases with natural gas added are directed to the tri-reformer. As a result, synthesis gas, raw material of chemical syntheses, is obtained. It should be stressed that direct CO₂ usage is assumed without its pre-separation, thus resulting in energy savings, since conventional method, such as CO₂-MEA absorption, requires high energy for absorbent regeneration [9, 12].

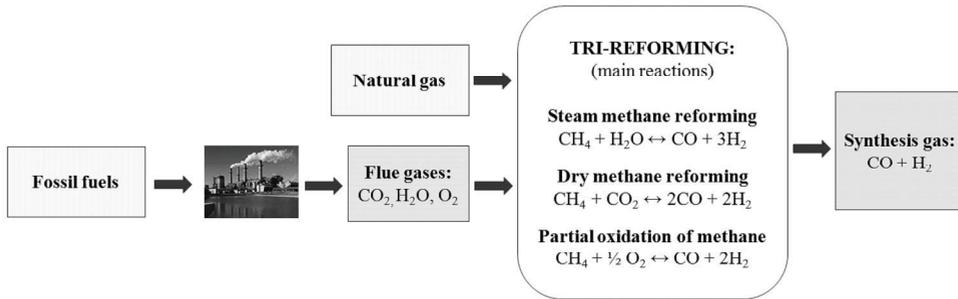


Fig. 3. Scheme of chemical CO₂ utilization by tri-reforming process implementation in coal- and gas-fired power stations.

As an example, for a typical coal-fired power station, ca. 20% of the produced energy (100 MW of 500 MW) should be used for the CO₂ capture via alkanolamines methods [10]. Tri-reforming would be also attractive for oxyfuel combustion due to high CO₂ content in flue gas.

Halmann and Steinfield [12] reported the possible CO₂ emission avoidance, as well CH₄ savings which could be gained, when syngas was produced via tri-reforming (instead of traditional steam reforming) with its following application to obtain typical bulk chemicals (methanol, ammonia, etc.), as illustrated by Fig. 4. The highest CO₂ emission avoidance (50%) occurs for methanol production. The largest fuel savings, however, are possible for hydrogen production.

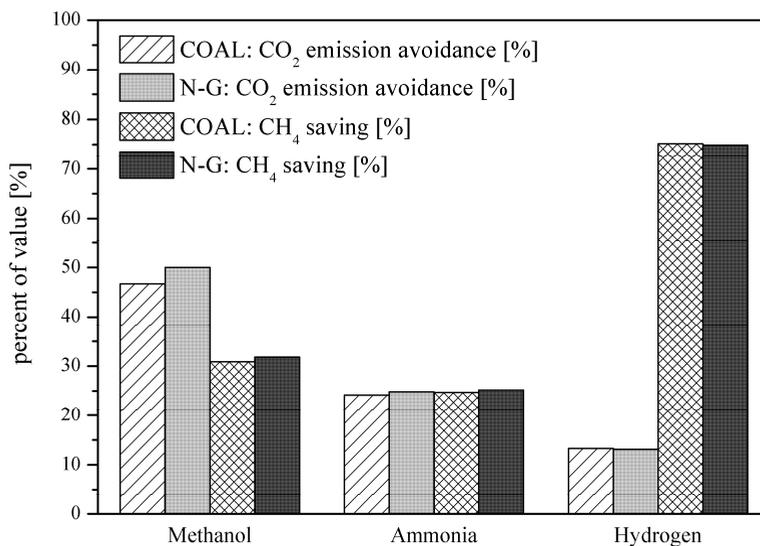


Fig. 4. Carbon dioxide emission avoidance and methane savings when methanol, hydrogen or ammonia are produced, with H₂ or syngas obtained via implementation of tri-reforming process in coal- and natural gas-fired power stations, instead of current industrial processes. The numerical data taken from [12]

2.1.2 Energy storage via TMR

Dry reforming of methane (DRM) is an endothermic reaction which may be used in the energy storage. The surplus energy (from renewable sources or off-peak) may be stored in either chemical products (e.g. methane, via methanation reaction) or used to power an endothermic process (such as e.g. DRM) and released via reversible exothermic reaction. This concept was widely described in literature [e.g. 6, 13, 14]. DRM, however, has certain disadvantages, of which the lack of stable catalyst is the most serious. DRM catalysts are prone to catalytic coking and thus shortened lifetime [6, 9]. In this respect tri-reforming would be of advantage, because the presence/addition of the H_2O and O_2 , as schematically shown in Fig. 5, would inhibit coke formation, and result in extended catalytic lifetime.

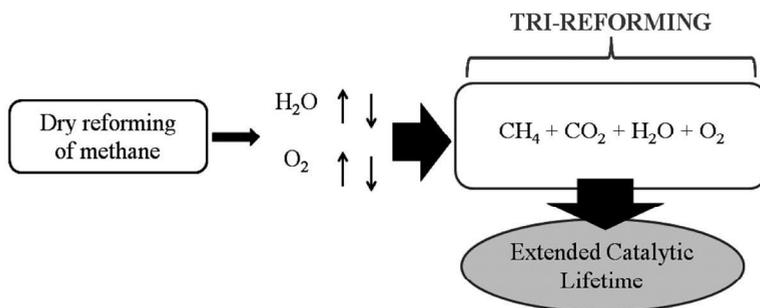


Fig. 5. Dry reforming of methane optimized by the addition of water and oxygen (tri-reforming process)

3 Catalysts for methane reforming process

The tri-reforming process requires an efficient catalyst. The required properties of the catalysts may be derived from mechanistic considerations.

Djéga-Mariadassou [15] considers the process as follows (* abbreviation for free radical):

- CH_4 is chemisorbed dissociatively on reduced metal Ni^0 (dry and steam reforming, partial oxidation of methane),
- CO_2 is activated via dissociative chemisorption; the used catalyst requires alkaline properties (dry reforming),
- H_2O activation with the formation of radical O and gaseous hydrogen (steam reforming),
- surface reactions are: (i) carbon radical $*C$ reacts with oxygen radical $*O$ (or hydroxyl radical $*OH$) in order to form CO of syngas, and (ii) two hydrogen radicals form hydrogen gas ($2 *H \rightarrow H_2$) via associative desorption (dry and steam reforming),

In case of partial oxidation of methane (POM), it has been shown by Djéga-Mariadassou [15] and Nishimoto et al. [16] that total CH_4 oxidation takes place on reduced metal: metal oxide MO (thanks to oxygen sites $O\square$), followed by dry reforming, and steam reforming (thanks to Ni^0). DRM proceeds satisfactorily either on precious metals (Pt, Rh, Ru, Ir) or metallic Ni, the latter preferred being much cheaper and more available [9]. SRM, the only process of the three reactions mentioned currently used on industrial scale, uses Ni based catalysts. The summary of TRM reactions and the required properties of possible catalysts, together with the proposed chemical component are presented schematically in Fig. 6.

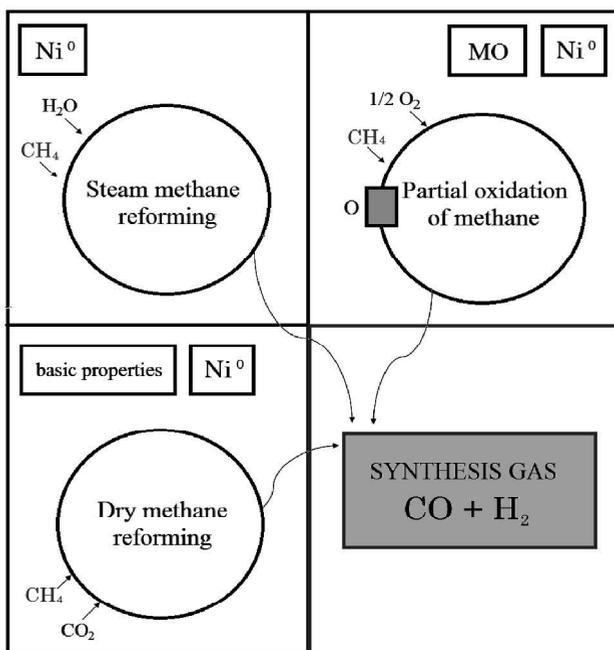


Fig. 6. Major components of TRM catalyst, based on: [15, 16]

3.1 Catalysts for single processes (SMR, DRM and POM)

Among three main tri-reforming reactions only the steam reforming of natural gas is the process on industrial scale. This reformation is focused on hydrogen production, and operates in the 700–1000°C, in the presence of nickel catalyst supported on alumina.

The dry methane reforming has not been yet implemented. The same as SRM, it shows very good properties with Ni as the active material. The newest DMR studies are mainly focused on stability increase due to the coke formation problem. Wide review was made by Dębek [6], as well as by Taniewski et. al [9]. The studied DMR catalysts were mainly Ni supported on Al₂O₃, MgO, CeO₂, ZrO₂, SiO₂, ordered mesoporous silica – SBA-15, La₂O₃, TiO₂, mixed oxides (MgO–Al₂O₃, CeO₂–ZrO₂, CeO₂–Al₂O₃), zeolites (zeolite Y, zeolite A, zeolite X, ZSM-5), clays (clinoptilolite, diatomite, vermiculite, montmorillonite), and carbon-based materials (carbon nanotubes, activated carbon). Several different promoters were tested: (i) alkali, or alkaline earth metals – K, Li, Mg, Ca, Ba, (ii) rare earth metals – Ce, Zr, La, and (iii) other metals – Au, Ag, Sn, Bi, As, Pb, Cu [6, 9]. Hydrotalcites (double layered hydroxides LDHs) were found to be especially interesting for DRM. These materials may contain Ni, Mg and Al in their structure, thus fulfilling the requirements for appropriate redox and basic properties. Dębek et al [17-22] showed that high CO₂ conversions may be obtained even at relatively low temperatures (around 600°C) with appropriate tailoring of Ni:Mg:Al composition and/or the addition of other structural elements, such as Zr, or promoters (Ce). The application of La as a promoter to Ni/Mg/Al hydrotalcites was also proven advantageous [23].

The partial oxidation of methane was also shown to be efficient for Ni-based catalysts, although the optimal support is still searched. The following oxides, or mixed oxides, were investigated as carriers [24]: Al₂O₃, MgO–Al₂O₃, MgO, CaO–Al₂O₃, CaO, BaO, SiO₂, CeO₂, ZrO₂, CeO₂–ZrO₂, SrO–La₂O₃, TiO₂, Mn₃O₄, perovskite oxides, SiC, ThO₂, Y₂O₃, Yb₂O₃,

alumina pillared bentonite, H-Y zeolite, ZSM-5 zeolite, active carbon, oxidized diamond, and more. In the literature of POM, also different promoters of Ni-based catalysts were considered: (i) noble metals – Pt, Pd, Ru, Ir, (ii) alkali, earth alkali metals – Na, K, B, Ca, Mg, Li, and (iii) rare earth metals – Ce, Zr, La, Y, Sm.

3.2 Catalysts for methane tri-reforming process

They are only scarce literature reports on catalysts investigated for TRM. Table 1 represents the examples of such catalysts, where the active component (Ni) was based on various supports: Al₂O₃ [25], ZrO₂ [26-28], SiO₂ spheres [11], β-SiC [29], CeO₂ [30], with or without the addition of promoter.

Table 1. Ni-based catalysts in tri-reforming of methane process

Support	Promoter	Results	Lit.
Al ₂ O ₃	Ce-ZrO ₂ ⁽¹⁾	Ce improved catalyst stability by increasing the mobility of oxygen ions on the surface	[25]
ZrO ₂	none	Strong interaction between Ni-ZrO ₂ = high activity; the best results for 4.8% Ni-loaded catalyst at 800°C	[26]
ZrO ₂	MgO ⁽²⁾	Mg improved CO ₂ adsorption = high activity; and increase of thermal stability	[27]
ZrO ₂	CaO ⁽²⁾	Samples with calcination at 700°C, and co-precipitated at pH of 10–12 gave the best catalytic results	[28]
SiO ₂ spheres	none	11% Ni/SiO ₂ showed stable activity at 750°C (4 hours) without deactivation. Presence of oxygen impacted coke formation and improved catalytic performance	[11]
β-SiC	Mg ⁽¹⁾	Adding Mg to the Ni/β-SiC (molar ratio Mg/Ni = 1/1) decreased coke formation, increased basicity, and improved Ni-Mg interaction. The sequence of Ni–Mg impregnation was important	[29]
CeO ₂	La ⁽³⁾	Adding La (10 at.%) resulted in strong interactions between Ni–La; Ce provided surface oxygen vacancies	[30]

¹⁾ impregnation, ²⁾ co-precipitation, ³⁾ combustion synthesis

Catalysts prepared by Lee et al. [25] contained Ni promoted with cerium and zirconium oxide on the alumina support. The major role was played weak acidic sites, basic sites, and redox abilities of Ce–ZrO₂. The catalyst displayed very good behavior by inhibition of the coke formation on the surface of catalyst, as well as on the reactor walls. The oxidant (steam or oxygen) had positive influence on the inhibition of carbon deposition, while the addition of cerium increased the mobility of oxygen ions on the catalyst surface.

Singha et al. [26] examined Ni supported on ZrO₂ without any additional promoter. It was noted that the rising Ni loading resulted in increasing Ni particle size. 4.8 wt.% Ni was reported as optimal for the used reaction conditions. High metal dispersion with strong metal support interaction (thanks to Ni–ZrO₂ presence) were found to be the most important factors in achieving high activity and stability.

Similarly observations were reported by Lai-Zhi et al. [27]. The catalyst with Ni-Mg-ZrO₂ exhibited strong metal–support interactions. The addition of Mg improved the alkaline character of the catalyst, and as a consequence improved CO₂ chemisorption. High temperature also has positive impact on the conversion of CH₄ and CO₂.

Other authors focused on the preparation conditions of the catalysts, such as pH of coprecipitation of catalyst and calcination temperature as factors which influence the catalytic performance. Lan-jie et al. [28] observed that after thermal treatment in the air at 700°C and the used preparation pH value of 10–12 it is possible to obtain proper surface area, nano-sized Ni particles, and very good Ni–ZrO₂ interaction which resulted in the more than 70% conversion of CH₄ (measurement at 700°C, 1 atm).

Majewski et al. [11] tested silica spheres which were covered by three-dimensional nickel. This resulted in shell structure which allowed the catalyst to encapsulate and protect nanoparticles via prevention of their migration during the catalytic reactions. The material was then called as nickel–silica core shell catalyst. In the catalytic tests an increase in oxygen content resulted in coke reduction and CH₄ conversion improvement (to 90%). The catalyst containing 11% Ni showed stable activity at 750°C (4 hours) without deactivation.

García-Vargas et al. [29] studied the influence of the impregnation order (of nickel and magnesium on silicon carbide SiC) on catalyst properties. Materials which had Mg impregnated in the first step were more stable and showed good catalytic performance. When Ni impregnation was the first step, weaker interaction between Ni and Mg was observed which, according to the authors, could have explained the blockage of Ni particles by Mg, the reduction of the number of Ni active sites and inferior catalytic results. It was additionally observed that the Mg/Ni molar ratio of 1/1 resulted in less coke formation, higher basicity, and better Ni-Mg interaction.

Pino et al. [30] studied Ni–CeO₂ materials loaded additionally with lanthanum (10 at.%). These catalysts showed strong interactions between Ni and La, and better Ni dispersion. Thanks to an appropriate amount of lanthanum loading, the CH₄ conversion increased from 93% to 96%, as well as CO₂ conversion 83% – 86.5%.

4 Conclusions

Tri-reforming of methane is the process consisting of steam reforming of methane, dry reforming of methane, and partial oxidation of methane. It may be considered as a method for the CO₂ emissions reduction, and as a process for synthesis gas production. The TRM might be implemented in the fossil fuels fired power stations, where natural gas together with pre-cleaned flue gases (SO₂, NO_x, and fly ash removed) are directed to the tri-reformer. Obtained syngas may be applied to produce chemicals and liquid fuels. The TRM application is a promising method due to high equilibrium (thermodynamic), possibility of converting CO₂ without its expensive pre-separation from flue gases, appropriate H₂/CO

molar ratios obtained, etc. TRM may be also applied as energy storage concept. Thanks to the H₂O and O₂ addition to the dry reforming system, it is possible to prevent coke formation on the surface of the catalyst. In addition, oxygen presence allows the production of heat in situ, thereby increasing process efficiency. However, it should be stressed that for the future implementation of tri-reforming on industrial scale, the active, stable (free from coke formation), and selective catalyst is a key requirement.

Nickel-based materials are widely used as catalysts for methane reforming processes due to availability and low price of this metal. They are an acceptable alternative for noble metals (Pt, Rh, Ru, Ir, Au) which are very expensive. Literature review for TRM shows that the reduced metal (Ni⁰) facilitates CH₄ dissociative chemisorption, therefore its presence is required in each of the reforming reaction. CO₂ chemisorption, on the other hand, requires basic sites, so the addition of elements of basic nature (e.g. Mg) is of the importance. Metal oxides (as support or promoters) play also an important role in case they offer oxygen sites allowing the oxidation of intermediates. Due to their structure and composition hydrotalcites (double layered hydroxides) containing Ni, Mg, Al and appropriate promoters may prove interesting materials for TRM.

Several types of single or mixed oxides were reported in the literature as possible supports for TRM catalysts: Al₂O₃, MgO, CeO₂, ZrO₂, SiO₂, La₂O₃, TiO₂. As promoters metals such as: Pt, Rh, Ru, Ir, Au, K, Li, Mg, Ca, Ce, Zr, La were reported to positively modify the catalyst structure. Their influence concerned: inhibition of carbon deposition, resistance to sintering of active phase, improvement the oxygen tolerance and its ions mobility on catalyst surface.

Acknowledgements to AGH 11.11.210.213

References

1. V. Bourgeois, M. Goll, *Eurostat news release*, **89** (2016), Available online on 23.08.2016: <http://ec.europa.eu/eurostat/documents/2995521/5176346/8-07052014-AP-EN.PDF/318b117b-2065-4a61-9efb-c382f901a8ea>
2. V. Bourgeois, M. Goll, *Eurostat news release*, **105** (2015), Available online on 23.08.2016: <http://ec.europa.eu/eurostat/documents/2995521/6875491/8-15062015-BP-EN.pdf/8adf74de-e79b-4778-905f-823c42c6e1b1>
3. L. Corselli-Nordblad, M. Goll, *Eurostat news release*, **74** (2014), Available online on 23.08.2016: <http://ec.europa.eu/eurostat/documents/2995521/5176346/8-07052014-AP-EN.PDF/318b117b-2065-4a61-9efb-c382f901a8ea>
4. J. Urhausen, M. Goll, *Eurostat news release*, **80** (2013), Available online on 23.08.2016: <http://ec.europa.eu/eurostat/documents/2995521/5166066/8-29052013-AP-EN.PDF/38dda41b-d760-4909-b8bd-77e651c401a3?version=1.0>
5. *Energy & climate change report*, Ed. OECD/IEA (2015)
6. R. Dębek, *Novel catalysts for chemical CO₂ utilization - Doctoral thesis* (2016)
7. Citizens' summary EU plan for a competitive low-carbon economy by 2050, Available online on 28.08.2016: http://ec.europa.eu/clima/citizens/summary/docs/roadmap_2050_en.pdf
8. G. Centi, S. Perathoner S., *Catal Today* **148**, 191 (2009)

9. M. Taniewski, T. Grzybek, J. Cetnar, Viable CO₂ chemical sequestration applications, in *Development of coal, biomass and wastes gasification technologies with particular interest in chemical sequestration of CO₂: a monograph* **99** (2015)
10. C. Song, W. Pan, *Catal Today* **98**, 463 (2004)
11. A. J. Majewski, J. Wood, *Int J Hydrogen Energ* **39**, 12578 (2014)
12. M. Halmann, A. Steinfeld, *Catal Today* **115**, 170 (2006)
13. J. H. McCrary, G.E. McCrary, T.A. Chubb, *Sol Energy* **29**, 141 (1982)
14. T.A. Chubb, *Sol Energy* **24**, 341 (1980)
15. G. Djéga-Mariadassou, *Catalysis for environment: depollution, renewable energy and clean fuels international annual meeting: proceedings*, 1 (2009)
16. H.-A. Nishimoto, K. Nakagawa, N.-O. Ikenaga, T.Suzuki, *Catal Lett* **82**, 161 (2002)
17. R. Dębek, A.Gramatyka, M.Motak, T.Grzybek, P.Da Costa, *Przemysł Chemiczny* **93**,2026 (2014)
18. R. Dębek, K. Zubek, M. Motak, P. Da Costa, T. Grzybek, *Research on Chemical Intermediates* **41**,9485 (2015)
19. R. Dębek, M. Radlik, M. Motak, M.E. Galvez, W. Turek, P. Da Costa, T. Grzybek, *Catalysis Today* 257, **59** (2015)
20. R.Dębek, K.Zubek, M.Motak, M.E.Galvez, P.Da Costa, T.Grzybek, *Comptes Rendus Chimie* **18**, 1205 (2015)
21. R.Dębek, M.E.Galvez, F.Launay, M.Motak, T.Grzybek, P.Da Costa, *International Journal of Hydrogen Energy* **41**, 11616 (2016)
22. R.Dębek, M.Motak, D.Duraczyńska, F.Launay, M.E.Galvez, T.Grzybek, P.Da Costa, *Catalysis Science and Technology*, **5**, 6705 (2016)
23. H. Liu, D.Wierzbicki, R.Dębek, M.Motak, T.Grzybek, P.Da Costa, M.E.Galvez, *Fuel* **182**, 9 (2016)
24. B. C. Enger, R. Lødeng, A. Holmen, *Appl Catal A-General* **346**, 1 (2008)
25. S.-H. Lee, W. Cho, W.-S. Ju, B.-H. Cho, Y.-C. Lee, Y.-S. Baek, *Catal Today* **87**, 133 (2003)
26. R. K. Singha, A. Shukla, A. Yadav, S. Adak, Z. Iqbal, N. Siddiqui, R. Bal, *Appl Energ* **178**, 110 (2016)
27. S. Lai-zhi, T. Yi-sheng, Z.Qing-de, X. Hong-juan, H. Yi-zhuo, *J Fuel Chem Technol* **40**, 831 (2012)
28. S. Lan-jie, W. Chang-zhen, S. Nan-nan, W. Xia, Z. Ning, X. Fu-kui, W. Wei, S. Yuh-an, *J Fuel Chem Technol* **40**, 210 (2012)
29. J. M. García-Vargas, J. L.Valverde, J. Díez, P.Sánchez, F. Dorado, *Appl Catal B-Environ* **164**, 316 (2015)
30. L. Pino, A. Vita, F. Cipiti, M. Lagana, V. Recupero, *Appl Catal B-Environ* **104**, 64 (2011)