The processes of hydrocarbon conversion using catalytic systems

A A Kuzhaeva, N V Dzhevaga and I V Berlinski
Saint-Petersburg Mining University, Russian Federation, Saint-Petersburg, 21st line, h. 2, 199106, Russia

E-mail: dzhevaga331@mail.ru

Abstract. This article describes properties of the catalytic conversion of methane to synthesis gas, makes a review of information on the chemical composition of catalysts and provides assumptions about the mechanism of their action. The facts and generalizations given in the article can be useful in determining ways to improve catalytic systems. The most active and most selective catalytic systems make it possible to optimize existing processes by cutting down energy consumption, cost, emissions and increasing the yield of a valuable product. Increasing the depth of conversion and the integrated use of raw materials, as well as ensuring the environmental cleanliness of the technological processes of processing is achieved by using highly efficient catalysts. With the help of highly efficient catalysts it is probable to increase the depth of conversion, the integrated use of raw materials as well as ensuring the environmental cleanliness of the technological processes of its processing.

1. Introduction
There are various ways of utilization of synthesis gas: firstly, to get liquid hydrocarbons and oxygen-containing compounds such as methanol, acetic acid, formaldehyde or dimethyl ether [1, 2]; secondly, in the industrial environment, its constituent, carbon monoxide (CO), is used for the synthesis of methanol (more than 50%), oxo synthesis products (15%), acetic acid (10-15%) (table 1). CO is necessary in herbicide production and pharmacy [3, 4].

Methane conversion, natural gas and other hydrocarbons being its sources, can result in getting synthesis gas of specific composition. Furthermore, effective processes of hydrocarbon processing – substrates of synthesis and anthropogenic origin, including substrates obtained from renewable biomass are given particular attention.

Practical concern for the purpose of rational use of industrial waste gas carbon and biogas carbon is development of methane and carbon dioxide joint processing. However, the task is complicated by high thermodynamic stability of CH₄ and CO₂ molecules complicates. Nonetheless, the two specified components belong to promising non-petroleum resources for the production of essential carbon-bearing products and hydrogen [5]. The basic method of natural gas processing is steam methane reforming.

| Product     | Required ratio H₂/CO, mol/mol | Production volume, kt/year (normal conditions) | Synthesis gas demand, km³/h |
|-------------|--------------------------------|-----------------------------------------------|----------------------------|
| Acetic acid | 0:1                            | 275 – 545                                     | 18 - 36                     |
| Methanol    | 2:1                            | 160 – 1,275                                   | 48 – 1,900                  |
2. Methods of steam methane reforming to synthesis gas
The only method of methane oxidative reforming, which is currently used in industry, is steam reforming method. The quantitative composition of formed synthesis gas in chemical reactions is different. Industrial use of synthesis gas of one or another composition determines its demand. Hence, for methanol synthesis the synthesis gas with 1:2 ratio is required [6, 7]:

\[ \text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}. \]

For production of ammonia from the nitrogen-hydrogen mixture, the synthesis gas with the composition of 1CO: 3H₂ is used on the production stage. Obtaining of synthesis gas with the ratio of 1:1 for the industrial production of diethyl ether corresponds to the equation [8, 9]:

\[ 3\text{CO} + 3\text{H}_2 = \text{CH}_3\text{OCH}_3 + 2\text{CO}_2. \]

However, in the conditions of this process, H₂O interacts with CO (CO steam reforming).

Significant difficulties in the practical realization of all methane reforming methods are connected with a thermal effect worthy of attention: both the endothermicity of steam and carbon dioxide reforming, and the exothermicity of partial oxidation result in the problem of heat supply or removal [10, 11].

A search for selective catalysts which permit to get useful products on purpose has been held for a long time, however, the problem has not been completely resolved. Consequently, research on catalysts, capable of selectively reducing methane, is still topical. In order to get the mechanism of the catalytic process and the possibility of its control one need to be aware of catalyst surface condition. Effective catalyst shall combine not only high activity but also high selectivity regarding the required product with high formation rate [12, 13], as well as maintain both properties throughout its working period [14 - 18].

When comparing catalyst properties relative to a specific chemical process, it should be noted that the use of selectivity implies that the reactions are related to a commensurate class [19-21], quasistationary in chemistry terms; otherwise, the description loses connection with the physical understanding of time.

Another crucial technological aspect concerns the side reactions of carbon formation that may take place when feeding the insufficient amount of water steam to the reforming installation. Coke production primarily deactivates the catalyst; then it results in the destruction of its granules, which in turn brings about partial or complete blocking of reaction flow in the catalyst layer that fills out the tube side. Hence, the local overheating sections appear.

The principal obstacle to the utilisation of different catalysts for methane reforming is their ease of poisoning by coke. Two ways of carbon formation during methane decomposition can be used [22-24]:

- methane dissociation
  \[ \text{CH}_4 = \text{C} + 2\text{H}_2 \]
  \[ \Delta H = +74.8 \text{ kJ/mole C} \]

- CO disproportionation, Boudouard equilibrium
  \[ 2\text{CO} = \text{C} + \text{CO}_2 \]
  \[ \Delta H = -172.5 \text{ kJ/mole C} \]

In reality, reactions occur at various temperatures: methane dissociation reactions take place mainly at high temperatures, Boudouard equilibrium - at low temperatures, and in real condition formation of coke almost always takes place. According to thermodynamic considerations, the total carbon deposition
shall decrease with temperature rise. The test confirms that the main quantity of carbon forms in accordance with methane dissociation reaction, but not Boudouard equilibrium. Often carbon diffuses to metal forming in the form of filaments at the catalyst discharge.

Methods of methane oxidation are various including homogeneous gas-phase oxidation, oxidation in the presence of heterogeneous catalysts, as well as photochemical and electrophilic oxidation [25-28].

Feedstock, namely natural gas and light hydrocarbons, is usually comprised of sulphurous components that shall be removed to prevent reforming catalyst poisoning.

In the conditions which are favourable to getting synthesis gas with low H₂/CO ratio, coke formation is much more likely to take place; therefore, the steam reforming catalyst shall be resistant to the processes of coke formation.

One of the ways to solve the problem can be the conduct of the steam reforming process that is passivated by sulphur. This process implements the idea of "ensemble control" by constant addition of sulphur that blocks active centres during coke; at the same time active centres of methane steam reforming are preserved. Such process requires careful dosage of sulphurous components and non-stop control over the performance of their functions. The utilisation of catalysts containing precious metals is effective as they are characterized by low coking [29, 30].

This survey is related to consideration of platinum-based catalysts, platinum being characterized by a number of features, platinum group metals, and some other d-elements.

3. Various scientific approaches to methane conversion using catalytic systems

The most effective catalysts are considered to be nanostructured systems; their active constituents contain particles commensurable with the range of action of interatomic forces in terms of dimensions. The current level of physicochemical methods’ development permits obtaining metals in the form of nanosized powders. The catalyst activity is increased thanks to the addition of metal nanopowders to zeolite which has become known due to a wide practical use of nanopowders for heterogeneous catalysis, namely methane carbon dioxide reforming to synthesis gas, methane and benzene deep oxidation, ammonia synthesis, Fischer-Tropsch process, carbon dioxide hydrogenation to methanol and others [31-36].

The ease of linear molecule passing to zeolite active centres, which have narrow channels, is explained by the so-called form-selective properties of mesomicroporous systems.

The basic requirements to catalyst carriers are their inertness, mechanical strength (abrasion), stability in reaction conditions and physical properties (specific surface, porosity, which is determined by the average pore size as well as the pore space distribution by radii) [37-39]. Aluminium, silicone, titan and zirconium oxides are considered to be the most widespread catalyst carriers that proved their effectiveness.

The “platinum on aluminium oxide” system is one of the most studied and widely applied in practice catalyst systems. Nonetheless, the examination of the mechanism of its formation is still topical. The traditionally used compound that is the precursor of active component in this system is chloroplatinic acid that is reversibly sorbed on the aluminium oxide surface. Consequently, on the ready-for-surface catalyst, the platinum centres that are not uniform by their condition are formed: some part is present in the form of disperse metal crystals, another part – in the form of charged clusters that are chemically bound with the carrier (ion platinum Pt°). One of the methods which handles the task of platinum stabilization in ion condition under the condition of high-temperature catalyst reduction treatment is the use of platinum hydroxo-complexes as precursor compounds. Their advantage is the possibility of strong metal attachment realization at the expense of OH-ligand complex exchange with aluminium oxide surface hydroxyl groups, which in this particular case plays the role of macroligand of some sort.

The improvement of carrier production technology happens for optimization of physicochemical properties and modification of the chemical composition of the carrier – aluminium oxide to get the following results at this stage:

- uniformly-porous system (increased selectivity);
percentage of 2-6 nm pores is not less than 90%;
- the total specific volume of pores is 0.6-0.65 cm³/g;
- specific surface (200-250 m²/g) should not change after regeneration – chlorine content (0.9-1.2 %) depends on it;
- Pt content not more than 0.25 % by weight;
- Pt dispersity is not less than 90 %.

Platinum metals in methane carbon dioxide reforming were more active than Fe, Co, Ni, and less exposed to carbon deposition because of lesser carbon solubility in these metals. Carbon dioxide reforming on these metals occurs with significant velocity even at 500 °C. However, high cost is the major and significant obstacle to their wide application. Ru and Rh are the most active among all metals, applied on Al₂O₃, MgO, ZrO₂ [40]. Ruthenium, rhodium and iridium catalysts are poisoned least of all, but their application is also unpromising due to their high cost. The activity was significantly increased by adding very small (0.02%) amounts of Pt, Pd and Ir to Ni₀.₀5Mg₀.₉₅O catalyst [41].

The addition of Ru to catalyst increases its activity to a great extent by the formation of bimetallic nickel-ruthenium clusters. At that, the more disperse Ni is obtained, which facilitates the formation of more reactive carbon. The search for noble metals applied on catalysts goes on. It is shown that Pt/ZrO₂, Rh/ZrO₂ and Rh/γ-Al₂O₃ are active and stable catalysts at 600 °C. The activity of Pt/ZrO₂ catalyst is determined by the accessible perimeter of applied platinum islands, whereas the activity of Rh/ZrO₂ and Rh/γ-Al₂O₃ is determined by the total number of rhodium atoms on the surface and thus does not depend on the carrier nature. Pt/SiO₂ activity is significantly lower.

Studies of CH₄ + CO₂ mixture reforming on Pt/ZrO₂ catalyst with the addition of molecular oxygen to the reaction system revealed the following results [42]. At 3.14% of O₂ and 800 °C the reaction rate increased slightly, yet at 550 - 750 °C the rate increased significantly (thrice at 550 °C and 14% of O₂) [43, 44]. At 11% of O₂ the reforming was constant for 30 hrs. In the absence of oxygen, the reforming decreased from 75 to 70%. ZrO₂ is believed to facilitate CO₂ dissociation permitting the removal of carbon, which results from CH₄ dissociation.

According to the results, one can conclude that catalysts in which metal is applied on oxides that are fixed composition phases deactivate rapidly, while the use of variable composition phases prevents catalyst deactivation, probably due to oxygen exchange at the phase boundary: gas-solid solution.

Chemical nature of carriers impacts on the catalyst activity and selectivity. The carrier nature mainly makes an impact on the crystal size and absorption heat, thereby influencing reaction parameters. There is information in accordance with which at the identical dispersity and selectivity the reaction is affected by the carrier acidity. Depending on differential carrier acidity, i.e. the ratio of Broensted and Lewis sites, catalysts which show various activity and selectivity are formed. The acid function of the carrier controls the formation of the metal active surface [45-51].

For improvement of the characteristics of catalyst system the following measures have been proposed:
- increase of platinum ion (non-metal) share. Consequently, the platinum activity in aromatization reactions increases 10-fold;
- Pt dilution by palladium (hydrogenolysis decrease);
- carrier surface treatment for the purpose of increasing its defect structure and getting "layered" platinum on it.

The applied catalysts are in need for metal dispersity increase for the acquisition of catalyst with more developed surface concurrently with small particles stabilization to prevent particle agglomeration.

The velocity of carbon dioxide methane reforming is proportional to CH₄ pressure raised to the power of one, while the pCΟ² value appears in kinetic equations, specified in various papers, in numerator and denominator raised to the power of n from 0 to 2 [52]. This indicates that methane interaction with the catalyst is the controlling step.
Comparative analysis of acid-base properties of titanium oxide, zirconium oxide, aluminium oxide and ferric phosphate surfaces with catalytic activity in papers [53] revealed that the substrate replacement and the method of its treatment (by water or organic solvent) lets changing the reaction direction. Modifiers with high molecular weight exercise the maximum influence on the carrier.

Activities of ruthenium catalysts on the carrier at natural gas complete oxidation changes as follows: Ru/Al₂O₃ > Ru/TiO₂ > Ru/SiO₂ > > Ru/ZrO₂. When studying the catalyst which consists of ruthenium chloride, applied on silica gel, the reduction of CO yield is discovered. It can be explained by the chloride ion impact on ruthenium state (at 600 °C — S(CO₂) selectivity = 100 %, and K(CH₄) reforming = 0.52). Hence, this catalyst can be characterized as more selective than metal ruthenium on SiO₂, but less perspective than Ru on Al₂O₃.

The analysis implies the exhaustion of the potential of applied systems. Still, according to the analysis of material used, variable composition oxides, used as carriers, prevent catalyst clogging due to carbonization processes; this direction of studies is still promising. The new generation of catalysts based on the Ni-(Co)-Mo-S system is likely to demonstrate its potential including the formation of surface nonstoichiometric compounds.

Recently there appeared an obvious interest in nanocrystalline (nanostructured) space structure systems that determine macroscopic ensembles of small particles up to several nanometres in size, coupled together in a certain way. Both structural features of separate particles and their collective behaviour determine the properties of materials; the collective behaviour depends on the character of interactions between particles. At that the crystal lattice of separate particles can be regular, defect and/or elastically stressed. It is possible to realize the coupling of separate elements via inter-crystalline boundaries which can have a different structure: quasi-amorphous, highly distorted crystal structure or with misfit dislocations, such as transition layer with other chemical composition, interphase boundaries.

4. Conclusion
The transition to nanosized metal particles was found to bring about changes in specific catalytic activity that is defined as a reaction rate in the presence of a catalyst, per the number of surface (available) atoms of metal. This relates to the emergence of size effect in structure-sensitive catalytic reactions, the rate of which modifies with the change of mean particle size of active component as opposed to structure-insensitive reactions. The study of size effects has become possible thanks to:

- evolution of controlled and reproduced methods synthesis of metal nanosized particles having similar and varied distribution of particles by size;
- evolution of methods for effective characterization of nanosized particles and determination of their distribution by size;
- study of catalytic properties and the comparison of values of catalytic activity depending on the mean particle’s size of applied metal particles;
- study of electronic, structure and adsorptive properties of nanosized metal particles depending on their sizes.

Getting of more active (specified particle size) and more selective (uniform distribution of particles by size) catalysts becomes possible thanks to positive changes in search of the factors, which stipulate the occurrence of size effects, and utilization of new synthesis methods, which give us an opportunity to obtain catalysts with tightly controlled properties. At the same time optimization of existing processes takes place by means of reduction of energy consumption (reaction temperature) and price indicators (decrease of noble metals load), the decrease of hazardous emission amount and the increase of valuable product yield.

References
[1] Liu D, Men Y, Wang J, Kolb G, Liu X, Wang Y and Sun Q 2016 Highly active and durable Pt/In₂O₃/Al₂O₃ catalysts in methanol steam reforming International Journal of Hydrogen
Effect of catalytic formulation on induced reforming of methanol. 

**Journal of Physics: Conference Series** 1399 (2019) 022057  
doi:10.1088/1742-6596/1399/2/022057

[2] Wang F, Li W-Z, Lin J–D, Chen Z–Q and Wang Y 2018 Crucial support effect on the durability of Pt/MgAl2O4 for partial oxidation of methane to syngas Applied Catalysis B: Environmental 231 292–8

[3] Schaber V M and Ivanova I V 2017 Prospects for Development of Fuel Cells Journal of Mining Institute 227 540–6

[4] Vita A, Italiano C, Ashraf M A, Pino L, and Specchia S 2018 Syngas production by steam and oxy-steam reforming of biogas on monolith-supported CeO2-based catalysts International Journal of Hydrogen Energy 43 (26) 11731–44

[5] Krilov O. 2000 Carbon dioxide conversion of methane to syn-gas. Russian chemical journal 1 19–33

[6] Wichert M, Zapf R, Ziogas A, Kolb G and Klemm E 2016 Kinetic investigations of the steam reforming of methanol over a Pt/In2O3/Al2O3 catalyst in microchannels Chemical Engineering Science 155 201–9

[7] Tahay P, Khani Y, Jabari M, Bahadoran F and Safari N 2018 Highly porous monolith/TiO2 supported Cu, Cu-Ni, Ru, and Pt catalysts in methanol steam reforming process for H2 generation Applied Catalysis A: General 554 44–53

[8] Dybkjaer J and Hansen J B 1997 Proc. IV Int. Natural Gas Conversion Symp. Kruger National Park, South Africa (Amsterdam: Elsevier) pp 99 – 116

[9] Pashkevich M A, Matveeva V A and Danilov A S 2019 Migration of pollutants from the mining waste disposal territories on the Kola Peninsula Gorny Zurnal 1 17–21

[10] Pena M A, Gomer J P and Fierro J L G 1996 New catalytic routes for syngas and hydrogen production Appl. Catal. A144 (1–2) 7–57

[11] Ioannides T and Verykios X E 1977 Proc. V Eur. Workshop on Methane Activation (Limerik, Ireland)

[12] Romanovskiy B V 2006 Basics of Chemical Kinetics (Moscow: Exam)

[13] Kazakova G D, Kozlova L V and Mardashev Yu S 1999 The dependence of the selectivity of deposited copper catalysts for oxidation of methane to formaldehyde on the nature of the initial salts and the carrier Russian Journal of Physical Chemistry A 73 (11) 1737–40

[14] Vass Á, Pászti Z, Bálint S, Németh P, Tompos A and Tálas E 2017 Structural transformation of Ga2O3-based catalysts during photoinduced reforming of methanol Materials Research Bulletin 95 71–8

[15] Palma V, Ruocco C and Ricca A 2018 Oxidative steam reforming of ethanol in a fluidized bed over CeO2-SiO2 supported catalysts: effect of catalytic formulation Renewable Energy 125 356–64

[16] Timonova O A, Kamenev A V, Kaziev G Z and Mardashev Yu S 2008 Enhancement of the efficiency of the process of mild catalytic oxidation of methane Petroleum Chemistry 48 (4) 322–3

[17] Dosumov K D, Popova N M, Baizhumanova T S and Tungatarova S A 2010 Selective oxidation of methane into synthesis gas at short contact times on low-loading platinum-ruthenium catalysts Petroleum Chemistry 50 (6) 455–61

[18] Grishina M A and Mardashev Yu S 2012 Prospects for the industrial use of methanol oxidation reactions Integrated Sientific Journal 3 71–3

[19] Timonova O A and Mardashev Yu S 2007 Inversion in selectivity of the methane oxidation under the influence of the support Russian Journal of General Chemistry 77 (12) 2214

[20] Timonova O A, Ivannikov D I and Mardashev Yu S 2009 Accounting for the "inflation" factor in the process of methane oxidation in a flow-through circulation system. News of universities. Chemistry and chemical technology 52 4 116–7

[21] Itkulova S S, Nurmakhanov Y Y, Kussanova S K and Boleubayev Y A 2018 Production of a hydrogen-enriched syngas by combined CO2-steam reforming of methane over Co-based
catalysts supported on alumina modified with zirconia Catalysis Today 299 272–9
[22] Nikolaeva N, Aleksandrova T and Romashev A 2018 Effect of grinding on the fractional composition of polymineral laminated bituminous shales () Mineral Processing and Extractive Metallurgy Review 39 (4) 231–4
[23] Zhao W, Chizallet C, Sautet P and Raybaud P 2019 Dehydrogenation mechanisms of methylcyclohexane on Αl2O3 supported Pt13: Impact of cluster ductility Journal of Catalysis pp 118–29
[24] Yang E, Jang E J, Lee J G, Yoon S, Lee J, Musselwhite N, Somorjai G A, Kwak, J H and An K 2018 Acidic effect of porous alumina as supports for Pt nanoparticle catalysts in: N –hexane reforming Catalysis Science and Technology 8 (13) 3295–303
[25] Liu S, Tamura M, Shen Z, Zhang Y, Nakagawa Y and Tomishige K 2018 Hydrogenolysis of glycerol with in-situ produced H2 by aqueous-phase reforming of glycerol using Pt-modified Ir-ReOx/SiO2 catalyst Catalysis Today 303 106–16
[26] Nikitenko S I, Chave T and Goff X L 2018 Insights into the Photothermal Hydrogen Production from Glycerol Aqueous Solutions over Noble Metal-Free TiO2 Core–Shell Nanoparticles Particle and Particle Systems Characterization 35 (10) 1800265
[27] Tálas E, Pászti Z, Korecz L, Domján A, Németh P, Szijjártó G P, Mihály J and Tompos A 2018 PtOx-SnOx-TiO2 catalyst system for methanol photocatalytic reforming: Influence of cocatalysts on the hydrogen production Catalysis Today 306 71–80
[28] Mills A, Bingham M, O’Rourke C and Bowker M 2019 Modelled kinetics of the rate of hydrogen evolution as a function of metal catalyst loading in the photocatalysed reforming of methanol by Pt (or Pd)/TiO2 Journal of Photochemistry and Photobiology A: Chemistry 373 122–30
[29] Zhao Z, Zhang L, Tan Q, Yang F, Faria J and Resasco D 2019 Synergistic bimetallic Ru–Pt catalysts for the low-temperature aqueous phase reforming of ethanol AIChE Journal 65 (1) 151-60
[30] Ruocco C, Meloni E, Palma V, van Sint Annaland M, Spallina V and Gallucci F 2016 Pt–Ni based catalyst for ethanol reforming in a fluidized bed membrane reactor International Journal of Hydrogen Energy 41 (44) 20122–36
[31] Dai R, Zheng Z, Sun C, Li X, Wang S, Wu X, An X and Xie X 2018 Pt nanoparticles encapsulated in a hollow zeolite microreactor as a highly active and stable catalyst for low- temperature ethanol steam reforming Fuel 214 88–97
[32] Li S, Tuel A and Meunier F J 2015 Platinum nanoparticles entrapped in zeolite nanoshells as active and sintering-resistant arene hydrogenation catalysts J. Catal. 332 25–30
[33] Dai C, Zhang S, Zhang A, Song C and Shi C, Guo X 2015 Hollow zeolite encapsulated Ni-Pt bimetal for sintering and coking resistant dry reforming of methane J. Mater. Chem. A 3 164–8
[34] Shi J, Li X, Wang Q, Zhang Y and Tang Y 2012 Platinum-encapsulated zeolitically microcapsular catalyst for one-pot dynamic kinetic resolution of phenylethylamine J. Catal. 291 87–94
[35] Zheng Z et al 2016 A novel BEA-type zeolite coreshell multiple catalyst for hydrogen-rich gas production from ethanol steam reforming Catal. Sci. Technol. 6 5427–39
[36] Ruocco C, Palma V and Ricca A 2018 Experimental and kinetic study of oxidative steam reforming of ethanol over fresh and spent bimetallic catalysts Chemical Engineering Journal 10.1016/jcej.2018.08.164
[37] Yan Y, Zhang Y, Jiang T, Xiao T, Edwards P P and Cao F 2017 Glycerol hydrogenolysis over a Pt-Ni bimetallic catalyst with hydrogen generated: In situ RSC Advances 7 (61) 38251–6
[38] Soares A V H, Perez G and Passos F B 2016 Alumina supported bimetallic Pt-Fe catalysts applied to glycerol hydrogenolysis and aqueous phase reforming Applied Catalysis B: Environmental 185 77–87
[39] Surendar M, Sagar T V, Raveendra G, Ashwani Kumar M, Lingaiah N, Rama Rao K S and Sai Prasad P S 2016 Pt doped LaCoO3 perovskite: A precursor for a highly efficient catalyst for
hydrogen production from glycerol *International Journal of Hydrogen Energy* **41** (4) 2285–97

[40] Oliveira É V, Seixas A C M and Jordão E 2017 Performance of Pt and Pt-Rh catalyst in the hydrogen production from glycerol *Canadian Journal of Chemical Engineering* **95** (10) 2018–23

[41] Erdohelyi A, Fodor K and Solymosi F 1997 *Proc. IV Int. National Gas Conversion Symp. Kruger National Park South Africa (Amsterdam: Elsevier)* pp 525–30

[42] Pendem C, Sarkar B, Siddiqui N, Konathala L N S, Baskar C and Bal R 2018 K-Promoted Pt-Hydrotalcite Catalyst for Production of H₂ by Aqueous Phase Reforming of Glycerol *ACS Sustainable Chemistry and Engineering* **6** (2) 2122–31

[43] O’Connor A M and Ross J R H 1997 Abstr. 5th *European Workshop on Methane Activation. Linerik Ireland*

[44] Bradford M C J and Vannice M A 1998 *J. Catal.* **173** 1 157–71

[45] Palma V, Ruocco C, Meloni E and Ricca A 2018 Oxidative reforming of ethanol over CeO₂-SiO₂ based catalysts in a fluidized bed reactor *Chemical Engineering and Processing (Process Intensification)* **124** pp 319–27

[46] Seretis A and Tsiakaras P 2016 Aqueous phase reforming (APR) of glycerol over platinum supported on Al₂O₃ catalyst *Renewable Energy* **85** pp 116–1126

[47] Safieva R Z, Stavitskaya A V, Safieva E O and Aleksandrova T N 2017 Hydrogenation of Unsaturated Hydrocarbons on Pt and Pd Catalysts Encapsulated in Mesoporous Bakelites *Chemistry and Technology of Fuels and Oils* **53** (4) 455–63

[48] Sodesava T 1998 *Kinetics and catalysis* **40** 3 452–3

[49] Palma V, Ruocco Meloni, E and Ricca A 2017 Highly active and stable Pt-Ni/CoO₂-SiO₂ catalysts for ethanol reforming *Journal of Cleaner Production* **166** 263–72

[50] Greluk M, Słowik G, Rotko M and Machocki A 2016 Steam reforming and oxidative steam reforming of ethanol over PtKCo/CoO₂ catalyst *Fuel* **183** 518–30

[51] Majrik K, Pászi Z, Korecz L, Trif L, Domján A, Bonura G, Cannilla C, Frusteri F, Tompos A and Tálas E 2018 Study of PtO₂/TiO₂ photocatalysts in the photocatalytic reforming of glycerol: The role of co-catalyst formation *Materials* **11** (10) 1927

[52] Bradford M C J and Vannice M A 1999 *Catal. Revs.* **41** 1 1–42

[53] Buffoni I N, Gatti M N, Santori G F, Pompeo F and Nichio N N 2017 Hydrogen from glycerol steam reforming with a platinum catalyst supported on a SiO₂-C composite *International Journal of Hydrogen Energy* **42** (18) 12967–77