Thermogravimetric Analysis of Carbon Based Catalytic on Decomposition of Methane

Vidyasagar Shilapuram[a], Nesrin Ozalp*[b]

[a]National Institute of Technology Warangal (NIT Warangal), Chemical Engineering Department, Warangal – 506 004, A.P., India
[b]KU Leuven, Mechanical Engineering Department, 3000 Leuven, Belgium
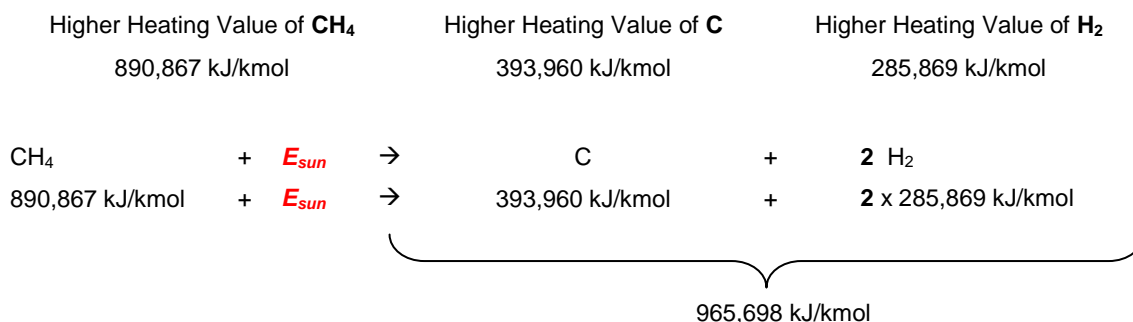nesrin.ozalp@kuleuven.be

Direct decomposition of methane offers two valuable products: hydrogen, and carbon black. However, methane is a stable molecule and its decomposition without catalyst requires temperatures of above 1,000 °C. There have been various transition metal catalysts used for methane decomposition in the past. However, using a metal catalyst is a major problem due to metal-carbon separation and catalyst deactivation because of carbon deposition on active sites. Therefore, carbonaceous catalysts have been the most efficient catalysts for direct decomposition of methane. The advantage of using carbon based catalysts is the low cost, the temperature and sulphur resistance, and no requirement of further separation of the catalyst. However, different physical characteristics of the carbon catalyst, including particle size, crystallographic structure, surface area, and the presence of surface groups, have direct effects on the kinetics of the reaction. By controlling such characteristics, methane decomposition can be optimized to achieve a higher production rate of hydrogen. This paper summarizes our extensive work on testing new as well as traditional carbon based catalysts via thermogravimetric analysis. Our results show that ordered mesoporous carbons are the most promising catalysts for methane decomposition.

1. Introduction

To oppose the rising levels of CO_2 emissions, it is essential to diversify fuel use by alternative fuels such as hydrogen. Currently, hydrogen is not widely used as a fuel. However, there is a substantial demand for hydrogen in the market as a commodity. While the chemical industry utilizes hydrogen as a feedstock to produce methanol, and ammonia; refineries uses it as the key feedstock in the hydro-treating and hydrocracking of hydrocarbons during crude oil processing (Ibrik et al., 2012).
Hydrogen is mainly produced by steam reforming of natural gas because of its economical attractiveness. However, steam reforming process releases substantial amount of CO_2/kg hydrogen produced. Because the process is endothermic, the heat is usually supplied by burning significant amount of the feedstock methane. To avoid environmental consequences and excess use of limited methane feedstock; there have been significant research activities to develop new methods for producing hydrogen.
One of the most promising hydrogen production methods is direct decomposition of methane via concentrated solar energy. Solar thermal decomposition of methane (or solar cracking) is a simple process where concentrated solar energy is directed to a reactor chamber in which CH_4 is injected and absorbs energy via convection and radiation. Solar energy is used to raise the methane to the necessary dissociation temperature and start the intensive endothermic process of cracking methane into hydrogen and carbon black. However, it should be pointed out that a substantial part of the energy content of natural gas cracking is captive in carbon. Therefore, with respect to the energy point of view, the majority of the natural gas energy content is not benefited if the carbon is not used as a fuel. If it is used as a fuel, the energy obtained from the products of methane cracking process vs. methane itself is:

Higher Heating Value of CH_4	Higher Heating Value of C	Higher Heating Value of H_2
890,867 kJ/kmol	393,960 kJ/kmol	285,869 kJ/kmol

CH_4 + E_{sun} →   C   +   **2** H_2

890,867 kJ/kmol   + E_{sun} →   393,960 kJ/kmol   +   **2** x 285,869 kJ/kmol

965,698 kJ/kmol

Therefore, if carbon is used as a fuel, then the products of solar cracking of methane provide more energy than methane itself, e.g. the total calorific value of the methane cracking products is 8 % higher than that of the methane since the cracking is an endothermic process.

Since methane cracking process does not emit any CO_2, there is no further energy and money spent on sequestration, storage and transportation of CO_2. However, it is crucial to make utmost use of carbon produced from methane cracking as it is essentially three times more than hydrogen production by mass. Most notable use of carbon in industry is to make batteries, rubber, conveyer belts, automotive tires etc.

Direct decomposition of methane requires very high temperatures of about 1,500 ºC. Such high operating temperature is the main concern to make solar thermally driven process compatible with existing solar concentrating technologies and to facilitate its large-scale implementation (Abanades et al., 2014). Therefore, it is important to find a solution to reduce reaction temperature without compromising from the conversion efficiency. This can be achieved by catalyst use.

Several prior studies investigated the effects of carbonaceous catalysts on the kinetics of methane decomposition reaction, using thermogravimetric analysis. These studies covered various commercially available carbon samples, and prepared carbon samples which have different textural properties. For example, Pinilla et al. (2008) observed that ultimate mass gain does not depend on the temperature but the type of carbon sample used. The change of activity of a catalyst as functions of time and reaction conditions of thermal decomposition of methane was presented by Abbas and Daud (2009a).

This paper summarizes the effect of various carbonaceous catalysts on direct decomposition of methane based on extensive Thermogravimetric studies.

2. Carbon catalysts used in methane decomposition

It is possible to use different types of catalysts in methane decomposition including metallic and carbon based ones. However, the use of carbonaceous catalysts is the most favourable option. This is because metal catalysts tend to rapidly deactivate and their regeneration requires a reactor shutdown. On the other hand, carbon particles absorb radiation from the reactor walls and convectively transfer that energy to the gas phase, which enhances the heat transfer and increases the methane conversion rate. Crystallographic structure, surface area, the presence of surface groups and energetic abnormalities are among major factors governing the catalytic activity of carbons. They do not require further separation from the product carbon, they are much less expensive than metal catalysts, and regeneration is not required.

Use of carbonaceous catalysts in direct thermal decomposition of methane was initiated by Muradov (1998), and it has been extensively studied since then both via using different reactor types and thermogravimetric analysis. Although laboratory scale reactors are being used to determine the kinetics, thermogravimetric analysis is considered advantageous. It is mainly because a small amount of catalyst is sufficient to identify the catalytic activity.

Various carbonaceous catalysts have been tested in direct thermal decomposition of methane such as activated carbon, carbon black, carbon fibres, carbon nanotubes, and graphite. For example, Ozalp and Shilapuram (2011) studied the carbon – hydrogen reaction to check whether the carbonaceous particles of the catalyst react with the hydrogen. Their results showed that carbon does not react with hydrogen to form methane or any other intermediate compounds up until 900 °C, which supports the favourable effect of carbon laden flow experiments for catalytic methane decomposition at lower temperatures. A later on study by Shilapuram and Ozalp (2011) demonstrated the catalytic characteristics of activated carbons Fluka-05105 and Fluka-05120 via thermogravimetric analysis observing higher threshold temperature for Fluka-05120. A more recent study by Shilapuram et al. (2014a) presents the deactivation kinetics of methane decomposition of these activated carbons, ordered mesoporous carbon, and ordered mesoporous carbide-derived carbon. A more detailed study by Shilapuram et al. (2014b) showed the catalytic activity of CMK-3 and DUT-19 as well. The results showed that these ordered

mesoporous/nanoporous carbons have better catalytic performance than commercially available carbonaceous catalysts.

Another example study focused on two different catalysts namely; palm-shell-based activated carbon (ACPS) manufactured from palm oil shells and commercial-based activated carbon (Abbas et al., 2009b). Both catalysts showed a reaction order of 0.5, and activation energy of 210 kJ/mol.

Pinilla et al. (2008) studied methane decomposition using carbonaceous catalysts. Their results showed the same reaction order of 0.5 for both catalysts, whereas activation energies of 141 and 238 kJ/mol were observed for CG Norit and BP2000. In a follow up study and Suelves et al. (2008) showed that BP2000 has higher capacity of carbon accumulation with 6.13 g deposition/gram of catalyst.

Serrano et al. (2010) and Botas et al. (2010) tested ordered mesoporous carbons CMK-3 and CMK-5. Their results showed that CMK-5 has higher reaction rate than CMK-3. Next section summarizes the details of the thermogravimetric experiments and results for various carbonaceous catalysts performance in methane decomposition.

3. Overview of thermogravimetric analysis results on catalytic methane decomposition

Our thermogravimetric methane decomposition experiments were done using Setsys Evolution 16/18, M/s; Seteram Instrumentation. Helium was used as a career gas whereas methane was used as the auxiliary gas. Flow rates of methane and corresponding volume percentages were selected in such a way that they fall within the accuracy limits of each mass flow controller. In most cases, 130 µL crucible made of 10 % Pt−Rh alloy was used. Each catalyst sample of known mass was loaded into the crucible and placed in the furnace. During this process, there is a chance that air may be trapped inside the furnace, which oxidizes the catalyst if it is not removed. Hence, a vacuum was created, and then the furnace was filled with the career gas. This cycle was repeated twice to ensure complete removal of air. Prior to the reaction, mass is stabilized by the flow of career gas under inert atmosphere. As the reaction took place, carbon from the methane decomposition was deposited in the crucible. This mass gain was recorded as a function of time. Activated carbon samples and the carbon deposition on crucible after the experiments were observed via SEM analysis to track changes as seen in Figure 1.

Three-zone experimental program was conducted based on temperature. The first zone was set to ramp the temperature with the rate of 30 °C/min. Reaction temperature was stabilized by carrier gas flow. This process also helped in desorbing any gases adsorbed on the catalyst during sample introduction. Auxiliary gas (CH_4) with the methane partial pressure of interest was then introduced into the furnace in the second zone while the carrier gas flow rate was simultaneously adjusted. Data was recorded up to 24 hours. This methodology was adopted for various reaction temperatures and inlet mole fractions of methane.

Our experiments involved mainly four different carbonaceous catalysts as follows: commercial catalysts Fluka 05120 and Fluka 05105; and in-house synthesized catalysts CMK-3 and DUT-19. CMK-3 was synthesized by infiltration of a solution of 2.5 g of sucrose, 0.28 g of H_2SO_4, and 10 g of water into 2 g of SBA-15 via the incipient wetness method (Figure 2a). DUT-19 was synthesized by using 1.42 g of SMP-10 (Starfire Systems) and 0.36 g of para-divinylbenzene added to 2 g of KIT-6 (Figure 2b). Properties of these catalysts are given in Table 1.
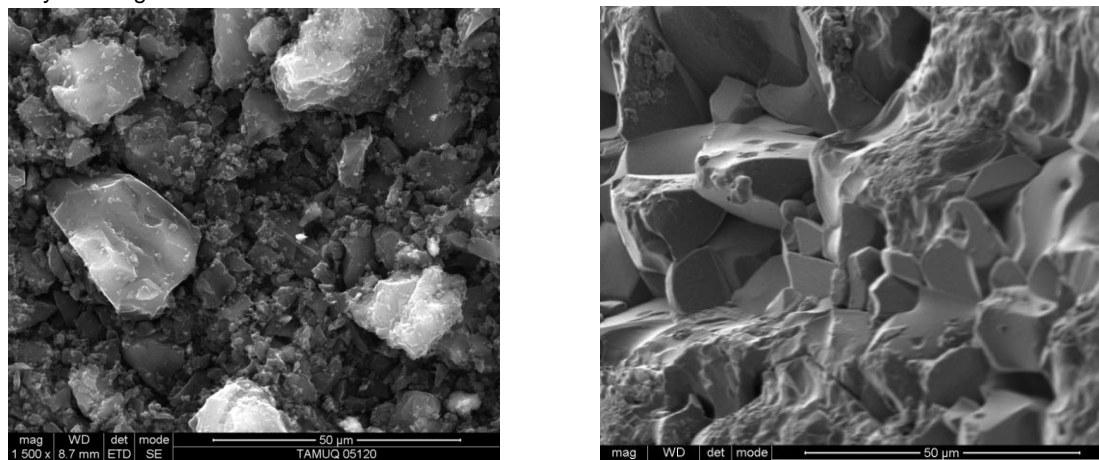

Figure 1: (a) SEM image of activated carbon (Fluka 05120) (Ozalp and Shilapuram, 2011a); (b) SEM analysis of lateral surface of carbon deposition on the crucible (Shilapuram and Ozalp, 2011b)

Table 1: Properties of the catalysts used in methane decomposition (Shilapuram et al., 2014a)

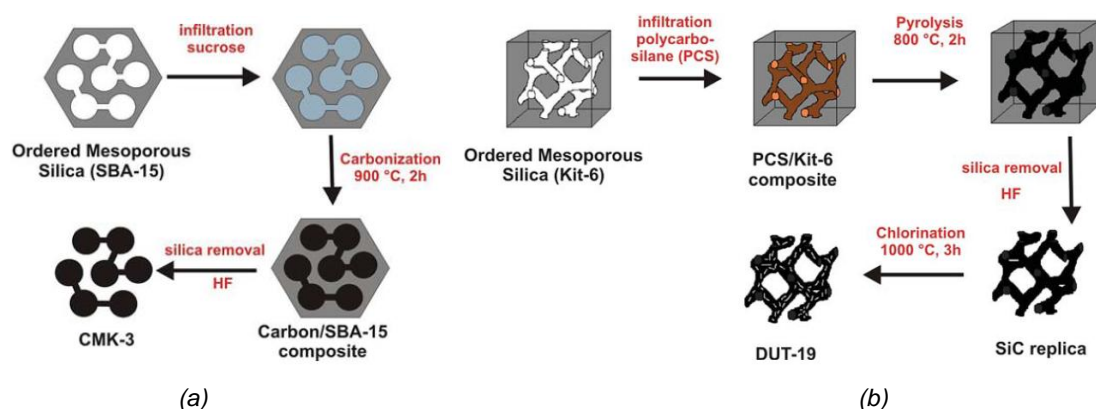| Catalyst	Particle size (µm)	Surface area (m^2/g)
Fluka 05120	891.6	46.1
Fluka 05105	890.1	33.6
CMK - 3	1400	NA
DUT- 19	2420	NA

(a)   *(b)*

Figure 2: Synthesis scheme for the preparation of CMK-3, (b) Synthesis scheme for the preparation of DUT-19 (Shilapuram et al., 2014b)

As seen in Figure 2 (a), sucrose was used as a precursor and silica with 2D hexagonal pore symmetry (SBA-15) was used as a template in CMK-3 synthesis. On the other hand, mesostructured carbide-derived carbons (DUT-19) were prepared via chlorination of the ordered mesoporous silicon carbide materials at 800 °C leading to the formation of additional micropores.

Because the threshold temperature is one of the main parameters for initial catalytic activity; experiments were conducted to find out the minimum temperature at which carbon formation rate is significant. The threshold temperature is the temperature at which the initial catalyst sample mass increases by 0.05 % due to carbon deposition as a result of methane decomposition. It can also be defined as the temperature at which initial catalyst sample weight increases by 0.5 % due to carbon deposition. It might be also defined as the temperature at which hydrogen production reaches 0.1 mmol H_2 per g of catalyst.

One of the main observations reported by Shilapuram et al. (2014a) was that carbon weight gain or carbon formation rate with time was a two zone phenomena for all catalysts. They reported that there was a rapid change in carbon weight gain in the first zone, whereas there was a rapid decrease in change of carbon weight gain and carbon formation rate.

In addition to experimentally observed carbon formation rate, the carbon deposition was also determined by thermodynamically predicted calculation as detailed in Shilapuram et al. (2014a). It was reported that the experimentally observed carbon formation was higher than the results found via thermodynamic calculation. It was because; thermodynamically predicted carbon deposition only defines the amount of deposition due to thermal methane decomposition. Therefore, the calculation does not take into account the use of a catalyst, the type of catalyst, or catalyst deactivation. Also, because there is a possibility that the autocatalyzed reaction might continue even after complete pore blocking of the catalyst, this leads to experimentally different result. There is also a possibility that the reaction might run on the outer surface of the blocked catalyst particles. It is known that after the very rapid initial blocking; the reaction continues for a long time. These are basically the main reasons for observing high carbon formation rates. A more detailed explanation on this difference was given in Shilapuram et al. (2014a).

Figure 3 shows carbon weight gain and carbon formation rate for the catalysts tested. Difference in reaction rates and ultimate weight gain were attributed to the differences in surface structure, single or bimodal pore distribution, the nature of agglomerated carbon formed, and the deactivation mechanism of the samples.
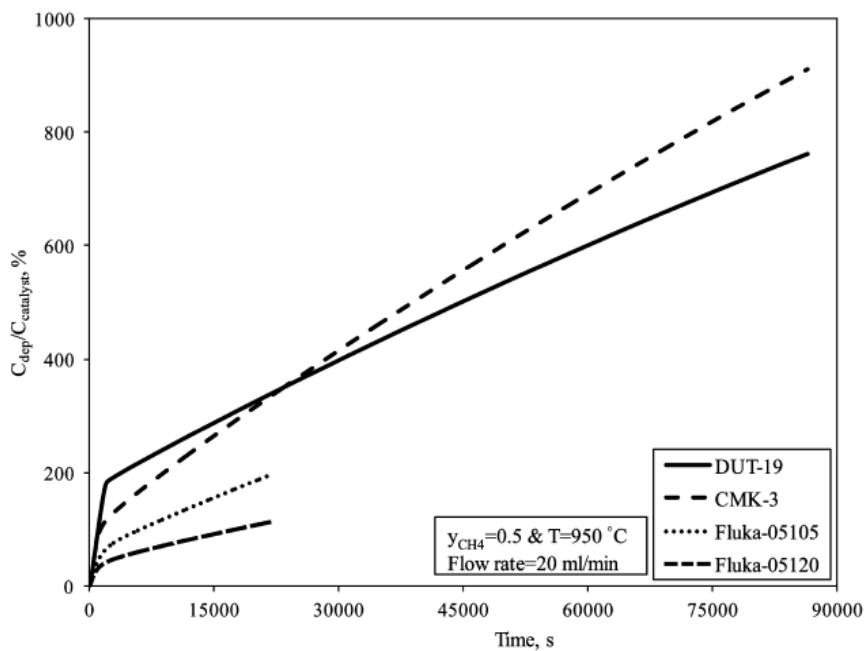
(a)
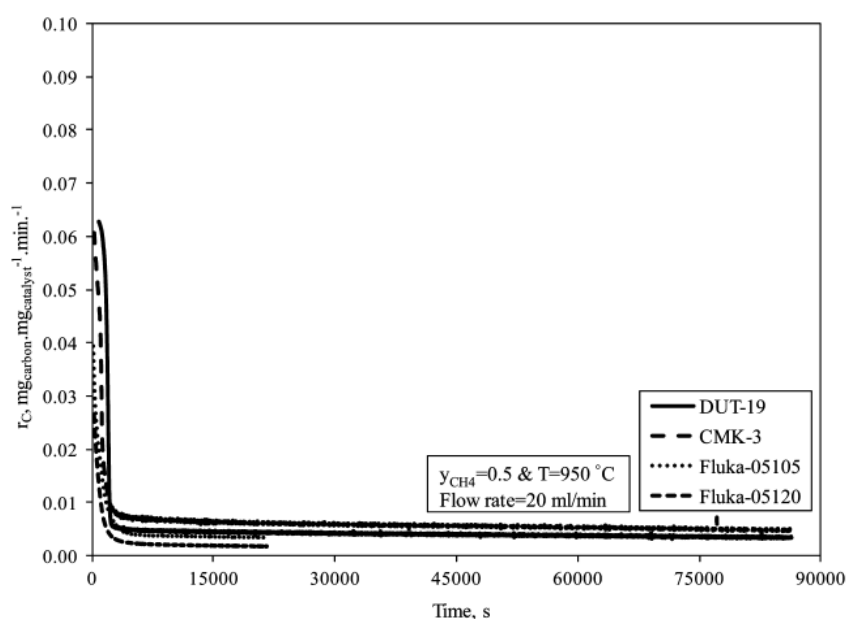
(b)

Figure 3: (a) Carbon weight gain, (b) Carbon formation rate (Shilapuram et al., 2014a)

Overall observation was the higher methane partial pressures lead to higher carbon formation rates. This implies that the methane decomposition was surface kinetics controlled. It was also noted that the reaction rate was dependent on the number of active sites of the catalyst sample because as carbon was deposited on the catalyst; the number of active sites were decreased as a result of catalyst deactivation. As very well known; carbon deactivation is one of the most important technical issues surrounding the industrial development of methane cracking based hydrogen production. It would be possible to control the catalyst deactivation by altering catalyst contact time. This would lead control of carbon nuclei and carbon crystal

growth formation. Control of catalyst deactivation would avoid carbon accumulation and may yield high reaction rates.

For industrial scale production of hydrogen via methane decomposition, the circulating fluidized bed technology may reduce catalyst consumption per mass of carbon produced due to the higher reaction rates achieved when controlling the deactivation of these materials.

4. Conclusions

An overview of catalytic decomposition of methane with carbonaceous catalysts was presented. Kinetics of these catalytic reactions as well as amount of carbon accumulated, carbon formation rate, and activity of the catalyst were determined via thermogravimetric analysis. Carbonaceous materials provide excellent catalytic activity in methane decomposition mainly due to their heat transfer characteristics in addition to high reaction rates. Additionally, because the catalyst and the product of methane decomposition are both carbon, regeneration and product separation are not required in the carbonaceous catalysed methane decomposition.

Thermogravimetric experiments showed that DUT-19 has the best catalytic properties of all the catalysts studied (Fluka-05120, Fluka-05105, CMK-3, and DUT-19) with higher carbon formation rate, carbon deposited, and average and cumulative hydrogen production. Specifically, DUT-19 has a lower threshold temperature and better catalytic activity compared to CMK-3; whereas Fluka-05105 demonstrates higher catalytic performance than Fluka-05120.

References

Abanades S., Kimura H., Otsuka H., 2014, Hydrogen production from CO_2-free thermal decomposition of methane: Design and on-sun testing of a tube-type solar thermochemical reactor, Fuel Processing Technology, 122, 153–162.

Abbas HF, Daud WMAW., 2009a, Deactivation of palm shell-based activated carbon catalyst used for hydrogen production by thermocatalytic decomposition of methane, Int J Hydrogen Energy, 34(15), 6231–6241.

Abbas H.F., Daud W.M.A.W., 2009b, Thermo-catalytic decomposition of methane using palm shell based activated carbon: kinetic and deactivation studies, Fuel Process. Technol., 90, 1167-1174.

Botas J.A., Serrano D.P., Guil-Lopez R., Pizarro P., Gomez G., 2010, Methane catalytic decomposition over ordered mesoporous carbons: a promising route for hydrogen production. Int. J. Hydrogen Energy, 35, 9788-9794.

Ibrik K., Al-Meer M., Ozalp N., 2012, Catalytic solar thermochemical processing for enhanced heat transfer and emission-free production of hydrogen, Chemical Engineering Transactions, 29, 499-504.

Muradov N.Z., 1998, CO_2-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel, Energy Fuels, 12, 41-48.

Ozalp N., Shilapuram V., 2011, Characterization of activated carbon for carbon laden flows in a solar reactor (Paper no. AJTEC2011-44381). Proc. 8-th ASME/JSME Therm. Eng. Jt. Conf., March 13-17, Honolulu, USA.

Pinilla J.L., Suelves I., Lazaro M.J., Moliner R., 2008, Kinetic study of the thermal decomposition of methane using carbonaceous catalysts, Chem. Eng. J., 138, 301-306.

Serrano D.P., Botas J.A., Fierro J.L.G., Guil-Lopez R., Pizarro P., Gomez G., 2010, Hydrogen production by methane decomposition: Origin of the catalytic activity of carbon materials, Fuel, 89, 1241-1248.

Shilapuram V., Ozalp N., Oschatz M., Borchard L., Kaskel S., LaChance R., 2014a, Thermogravimetric analysis of activated carbons, ordered mesoporous, carbide-derived carbons and their deactivation kinetics, Industrial & Engineering Chemistry Research, 53(5), 1741-1753.

Shilapuram V., Ozalp N., Oschatz M., Borchardt L., Kaskel S., 2014b, Hydrogen production from catalytic decomposition of methane over ordered nanoporous carbons (CMK-3) and carbide-derived carbon (DUT-19), Carbon, 377-389.

Shilapuram V., Ozalp N., 2011, Carbon catalyzed methane decomposition for enhanced solar thermal cracking (Paper no. ESFuelcell2011-54644). ASME 5-th Int. Conf. Energy Sustainability, Proc., August 7-10, Washington DC, USA.

Suelves I., Pinilla J.L., Lázaro M.J., Moliner R., 2008, Carbonaceous materials as catalysts for decomposition of methane. Chem. Eng. J., 140, 432-438.