



Methane decomposition kinetics on unfunctionalized alumina surfaces

T. Kreuger^a, W.P.M. van Swaaij^a, A.N.R. Bos^{b,c}, S.R.A. Kersten^{a,*}

^a Sustainable Process Technology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

^b Laboratory for Chemical Technology, Ghent University, Technologiepark 125, Ghent 9052, Belgium

^c Shell Global Solutions International B.V., P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

ARTICLE INFO

Keywords:

Thermal decomposition
Methane
Pyrolysis
Hydrogen
Syngas
Kinetics

ABSTRACT

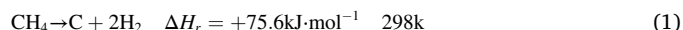
The pyrolytic conversion of methane for the production of hydrogen and carbon was investigated over nonporous α -Al₂O₃ surfaces in the range of 900–1300 °C. Two devices were used: i) a single particle reactor to determine the carbon deposition rate at various temperatures and ii) a fixed bed in which both methane conversion and carbon deposition were measured.

It was observed that at 1000 °C and below, the selectivity towards carbon (and hydrogen) was initially low over fresh α -Al₂O₃ (e.g. 38% at 250 s reaction time), increasing to 100% over time. Methane conversion was constant at 20% during this period. These observations point towards the presence of an activation process for the formation of carbon and hydrogen from the intermediates products (e.g. benzene) of methane pyrolysis. A temperature dependent maximum in carbon loading was observed. When this maximum carbon loading was reached, methane conversion also stopped completely, indicating 100% selectivity towards carbon and hydrogen.

Two kinetic models for carbon deposition were derived and applied. After parameterization of these models using single particle data, they were able to predict carbon growth and CH₄ conversion as function of temperature, specific bed area, carbon loading and gas composition in the new data set from the fixed bed.

1. Introduction

Recently, the decarbonization of fossil fuels has received increased interest [1]. The pyrolysis of CH₄ into carbon and hydrogen is an example of a decarbonization reaction:



Deposition of solid carbon means that no CO₂ is emitted, and the carbon is readily separated. The pyrolysis of methane occurs at elevated temperatures [2,3]. Typical decomposition temperatures range from 500–1000 °C for metallic catalysts [4,5] and 850–1300 °C for unfunctionalized ceramic carriers [6,7]. Pressures range from 1 bar CH₄ and higher. The solid carbon may be gasified again to CO to yield synthesis gas. Three types of catalysts are reported upon in literature: metal based [8–11], carbon based [12–17] and unfunctionalized carriers [16,15]. Literature is widely available for metal and carbon catalysts. These works show a decrease in required temperature to achieve methane conversion. However, a large part of these works show a relatively fast deactivation of the catalyst, either during carbon deposition or after

gasification of the deposited carbon [9,10,12–15]. In other cases, up to 10 carbon deposition–gasification cycles are reported without significant activity loss [8].

The main advantage of unfunctionalized carriers is the stability, being inert up to high temperatures in a large range of atmospheres. This work will focus exclusively on the decomposition part, however. Because a large variety of carrier materials is present, a selection had to be made. An initial choice was made for Al₂O₃ as it is a common carrier that is widely available. Other materials are evaluated in future work.

During the pyrolysis of methane, carbon is deposited on a surface in the reactor. It is generally accepted that the formation of solid carbon from methane is achieved via the formation of acetylene and benzene [18,2,19]. The simplified reaction network is a stepwise dehydrogenation: CH₄ → C₂H₆ → C₂H₄ → C₂H₂ → C₆H₆ → C. Several authors have proposed more expanded reaction networks consisting of hundreds of reactions [19–21].

Analysis of the carbonaceous deposits after CH₄ pyrolysis showed that numerous polyaromatic hydrocarbons are present in the deposited material [22]. Many authors report on the decomposition kinetics, [23,24,2,25–28,15,29,30]. However, the majority of those focuses on the first steps of the methane decomposition and designed the

* Corresponding author.

E-mail address: S.R.A.kersten@utwente.nl (S.R.A. Kersten).

<https://doi.org/10.1016/j.cej.2021.130412>

Received 12 March 2021; Received in revised form 12 May 2021; Accepted 16 May 2021

Available online 23 June 2021

1385-8947/© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Nomenclature		p	Particle, phase
Greek Symbols		r	Reactor
ϵ	Void fraction $\text{m}^3.\text{m}^{-3}$	Variables	
ρ	Density $\text{kg}.\text{m}^{-3}$	A	Surface area $\text{m}^2.\text{g}^{-1}, \text{m}^2.\text{m}^3$
σ	Error $\text{mol}.\text{m}^{-2}$	C_X	Concentration of species X $\text{mol}.\text{m}^{-3}.\text{mol}.\text{m}^{-2}$
τ	Residence time in hot zone s	D	Diameter m
Subscripts		E_a	Activation energy $\text{J}.\text{mol}^{-1}$
AS	Available site	F_X	Flux of species X $\text{mol}.\text{m}^{-2}.\text{s}^{-1}$
C	Carbon	k	Kinetic rate constant
dec	Decomposition	L	Length m
exp	Experimental	M_C	Molar weight carbon $\text{kg}.\text{mol}^{-1}$
ex	External	n	Number of datapoints
g	Gas	p	Polynomial coefficient
H	Hydrogen	RR	CH ₄ reaction rate
mod	Model	S	Selectivity
M	Methane	t	Time s
m	Mass transfer	u_g	Superficial gas velocity $\text{m}.\text{s}^{-1}$
nuc	Nuclei	x	Volume fraction

experiments so that little to no carbon was formed in the system, they exclusively studied the step towards gaseous hydrocarbons. To advance process development a kinetic model describing carbon deposition as function of temperature, pressure, gas composition and particle characteristics is required. As far as we know, such a model is not available. This paper describes an attempt to develop a kinetic model for carbon deposition during methane pyrolysis on non-porous α -Al₂O₃. The model is based on experimental data of carbon deposition collected for this paper and reported mechanistic studies [31,32,26,28,23,33]. Non-porous particles offer the advantage that internal mass transfer effects can be excluded. In upcoming work, we will report on various porous particles. It was our strategy to use a single particle reactor and a fixed bed reactor. The single particle reactor was designed so that carbon deposition was not hindered by mass transfer limitations and it allowed precise control of the reaction temperature. Next to that, interpretation of the single particle reactor data was not hindered by heating and cooling trajectories of the particle, spatial gradients in gas composition or wall effects. In the fixed bed, the coupling between carbon deposition and methane conversion could be studied. The fixed bed was also used to investigate if the kinetics derived from single particle data could predict results obtained in the fixed bed.

To the best of our knowledge, we are the first to report detailed (kinetic) data on carbon deposition from methane pyrolysis on non-porous particles.

2. Materials and methods

2.1. Materials

Two types of nonporous α -alumina particles were used in this work. Particle A (1.5 mm diameter, 99% Al₂O₃, $\rho_p = 3740 \text{ kg}.\text{m}^{-3}_p$) was obtained from Saint-Gobain NorPro. Particle B (3 mm diameter, 99% Al₂O₃, $\rho_p = 3688 \text{ kg}.\text{m}^{-3}_p$) was obtained from Baan Machines. Si₃N₄ precision spheres (Nonporous, 3 mm diameter, Ra surface roughness 12 nm) were obtained from Ceratec Technical Ceramics. In this work, all the particles were used as received, additional details on the used particles are presented in Table 7 in appendix A. Methane (99.999%) was supplied by Linde. Nitrogen (99.999%) was supplied by Nippon Gasses. Calibration gasses, hydrogen, oxygen and shielding gas (95% Ar, 5%H₂) were supplied by Linde. All gasses used in this work were used as received.

2.2. Heating unit

Heating of the reactors was facilitated by an in-house constructed radiation oven (max. temperature 1500 °C). The temperature was controlled using Eurotherm P116 controllers in the 2 heaters (16 cm axial length each) individually. A cross section of the heating unit internals is presented in Fig. 1b. Heating was provided by heating wires (1.5 mm diameter, SuperKanthal A1, Salomons Metalen) wrapped around a cylindrical radiation element (99.7% Al₂O₃, Haldewanger). The inner diameter of the radiation element was 30 mm. The radiation element was placed inside the oven vertically. The reactor tube was placed inside this element, so that radiation reached the reactor tube all around. In this reactor tube the single particle reactor (Section 2.3) or the fixed bed (Section 2.4) was placed. The controlling type S thermocouples were placed on the outside of the reactor tube wall, inside the radiation element. The axial height of the controlling thermocouples depended on the experimental configuration used and is discussed in the following sections. All the internals were isolated with alumina wool (Morgan Ceramics) and placed in an aluminium enclosure. A detailed list of construction materials is included in appendix A, Table A.6.

2.3. Single particle configuration

In the single particle reactor an Al₂O₃ particle was suspended in a CH₄ flow by placing it in a conical reactor. A reactor tube (11 mm ID, 99.9% Al₂O₃, Haldewanger) was placed inside the oven. The conical Al₂O₃ reactor was placed inside this reactor tube, as presented in Fig. 1b. In Fig. 1c a schematic of the cone itself is presented. At the bottom of the cone the local gas velocity equaled the terminal velocity of the particle, thereby suspending the particle inside the cone.

To check the mass transfer around the particle, the carbon deposition rate was compared to the carbon oxidation rate, which is most likely mass transfer limited. To measure the oxidation rate a carbon loaded particle was suspended at 1000 °C in air. The oxidation rate measured was a factor 100 faster than the carbon deposition rate during pyrolysis, therefore the carbon deposition rate cannot be mass transfer limited. An additional study into the mass transfer in the cone has been performed using the sublimation of a copper particle, this is presented in appendix C and supports that the methane decomposition is not mass transfer limited.

The temperature was controlled by placing the type S control thermocouple at the height of the cone. The controlling thermocouple for

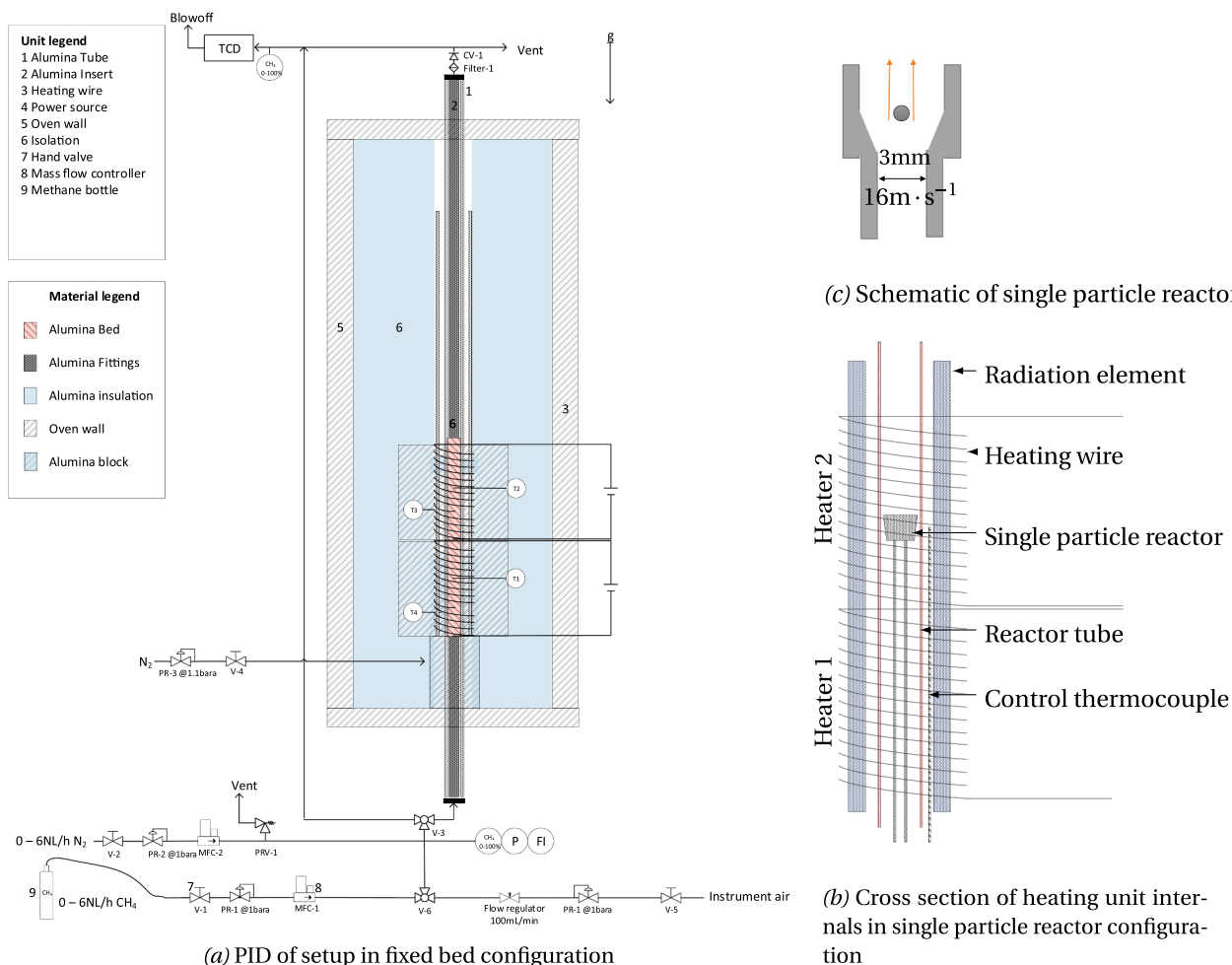


Fig. 1. Overview of the experimental setup.

this first heater was placed halfway along the axial length of the first heater. For measurement accuracy it was important to know the particle temperature. For this, an energy balance was made, taking into account energy consumption by the decomposition reaction and energy inflow via radiation. This energy balance assumes the gas had reached the setpoint temperature before it reached the particles height within the cone, and therefore no energy was transferred between gas and particle. The energy balance is presented in [appendix B](#), and shows that the particle temperature does not deviate from the setpoint temperature significantly. Hence, the decomposition reaction is not heat transfer limited.

To ensure the gas had heated up to the setpoint temperature, the energy consumption of the second heater was monitored with and without gas flowing through the cone. A detailed explanation of this is presented in [appendix B](#). If the second heaters power consumption did not change when the gas was turned on, the gas had reached setpoint temperature when it reached the cone. This was ensured by gradually increasing the setpoint of the first heater, thereby increasing the gas temperature. The difference in power consumption of the first heater with and without gas flow was approximately 70 W, in agreement with the theoretical power required to heat the CH_4 stream to setpoint temperature.

When the particle was contacted with methane, a carbonaceous material was deposited on the particle, increasing its mass. Since this particle was not in contact with any reactor wall, effects of surfaces other than the particle were ignored. Via the mass change over time the carbon deposition rate was obtained. As gas residence time was in the order of 1 ms and the surface to volume ratio was very low, the measured CH_4

conversion was negligible, as confirmed by GC. The deposited carbonaceous material will contain a small amount of hydrogen. Literature on pyrolytic graphite deposited from methane at higher temperatures than this work show a H/C ratio of $0.0004\text{ mol}\cdot\text{mol}^{-1}$ [34]. The carbon in this work is deposited at lower temperature, and should therefore have a higher H/C ratio [34,35]. However, the H/C ratio would have to be 3 orders of magnitude higher than this literature value in order to significantly change the mass of our deposited material. Therefore, the hydrogen in the carbonaceous material is neglected.

For more enhanced experimentation, it was investigated whether it was possible to introduce up to 3 particles simultaneously into the reactor. In [appendix A](#), Table A.9 it is shown that comparable carbon loadings are found, regardless of the number of particles. Therefore, for most of the experiments 3 particles were used simultaneously.

2.3.1. Experimental procedure

With the cone present in the reactor tube the system was heated to setpoint (Heating rate $10\text{ K}\cdot\text{min}^{-1}$) under nitrogen. When setpoint was reached, the CH_4 flow was turned on. Inflowing gas had a flow rate of 1600–1800 NmL/min. This was controlled by a mass flow controller (Brooks) and was varied depending on the setpoint temperature. Superficial gas velocity through the cone base was kept constant over all experiments. After passing through the reactor the gas was vented. When the system had reached steady state (as measured by heater power consumption) a particle was introduced by opening the top valve. The particle fell into the cone and remained there until the desired time was reached. This was confirmed visually via an observation port in the top of the setup. The addition of carbon onto the particle did not affect the

suspension of the particle, as the deposited amounts were relatively small. After an experiment the gas flow was turned off. The particle fell through the Al_2O_3 tube and was collected in a 5 ml sample glass connected to the reactor. The particle cooled down in ± 1 s, as confirmed by measurements using an IR camera, no active cooling was required. Afterwards the carbon content was calculated via the weight difference and the sample was stored.

2.3.2. Reproducibility of experiments

To test reproducibility and to establish the measurement uncertainty, two test series were done. The first series composed of repeating a deposition test under identical conditions a number of times using different particles from the same batch. The found standard deviation on the mean was 6%. In the second series, three particles were suspended in a CH_4 flow at 1100°C for 20 min. The carbon mass fraction was measured, and the carbon was burnt off under pure oxygen at 1100°C for 6 h. This was repeated 5 times. The results of this series are listed in Table 1. Also for this series, the standard deviation on measurement mean was 6%.

Hence, repeated usage of a single particle compared to single use of multiple particles did not increase accuracy. It was decided, for efficiency reasons, to repeat each condition several times using different particles. Because of the large spread each measurement was repeated 12 times or more, to obtain an acceptable confidence interval.

2.4. Fixed bed configuration

The fixed bed was placed inside the reactor tube (Fig. 1a). The axial location of the controlling thermocouples was the axial middle of heater 2 which coincided with the axial middle of the bed. The control thermocouple was placed outside the reactor tube, within the heating element, as in Fig. 1b. During some experiments, temperature measurements were performed inside the reactor. For this, an Al_2O_3 insulated type S thermocouple (3 mm OD, 600 mm length) was inserted into the reactor tube. At the controlling thermocouple axial height, measured temperature did not deviate from the setpoint temperature by more than 2°C , which is less than the accuracy of the used thermocouple at this temperature. Moreover, along the complete axial length temperature did not deviate over time. Therefore, temperature is regarded as constant over time, but not over axial length, as a temperature profile is present throughout the bed (presented in Fig. 5). For the experiments where internal temperature measurements were performed, a reduction in bed volume and area occurred because of the thermocouple, therefore these datapoints were not included in the final dataset.

Inflowing gas was CH_4 and N_2 with flow rates ranging from 0–100 $\text{NmL}\cdot\text{min}^{-1}$. These were controlled individually by mass flow controllers (Brooks). By changing the gas flow rate residence times in the bed were varied between 0.2 and 2.5 s. Gas entered the reactor through the bottom coupling. Before and after the bed, cylindrical (OD 10 mm) Al_2O_3 inserts were placed in the reactor, decreasing dead volume outside the bed. Total axial bed length was 40 cm and kept constant over all experiments.

Methane fractions were measured every 1.2 s using IR sensors (0–100%vol CH_4 , MIPEX). The CH_4 sensors were placed before and after the reactor. Hydrogen fraction was measured using a TCD (Caldos 5G-Ex), at the reactor outlet. Both the CH_4 and H_2 sensors were calibrated

Table 1

Carbon loading after repeated experiments in the single particle reactor, particle A.

Run number	Measured loading [$\text{g}\cdot\text{m}^{-2}\cdot\text{p}_{\text{ex}}$]				
	1	2	3	4	5
Particle 1	17.9	20.9	17.9	19.4	16.4
Particle 2	24.8	26.1	24.8	24.8	23.4
Particle 3	18.0	22.1	21.1	21.1	21.1

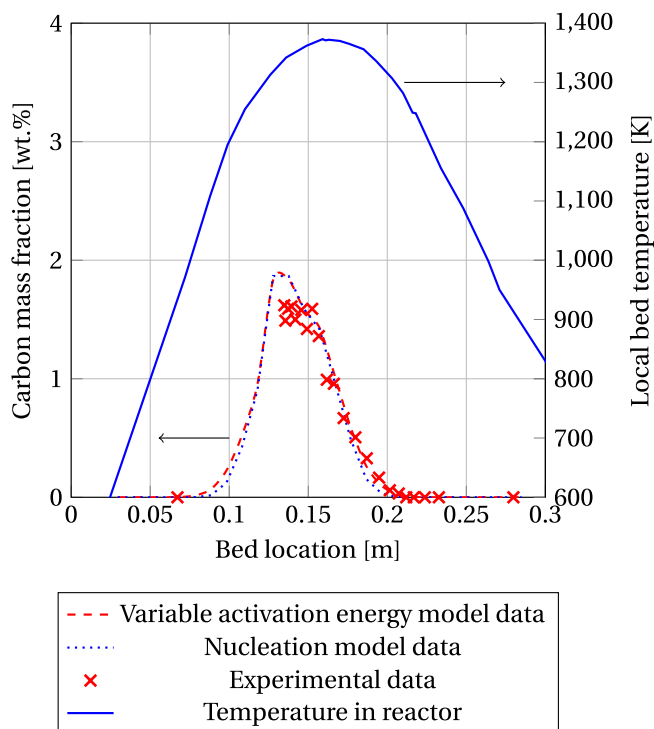


Fig. 5. Carbon and temperature profile measured in fixed bed reactor. Setpoint 1100°C , total runtime 1800 s, Gas residence time 0.6 s, Inlet fraction $\text{CH}_4 = 0.5$, particle A.

using pre-mixed gasses (Linde). Pressure was measured at the reactor inlet (Brooks SolidSense II), the reactor outlet was at atmospheric pressure at all times. All relevant measurements were corrected for changes in atmospheric pressure over time. Inlet flow was measured using a Brooks mass flow meter. After analysis the reactor offgas was vented. For GC measurements, samples were taken by hand using a 50 ml syringe during selected experiments.

2.4.1. Experimental procedure

Before each experiment, the inner reactor wall was cleaned with a steel brush. The reactor was then rinsed with acetone and demineralized water, and dried by blowing compressed air through the tube. The reactor was filled with the inserts and fresh bed particles. The bed was flushed with a $100\text{ NmL}\cdot\text{min}^{-1}$ N_2 flow during heating and cooling of the reactor.

The heating rate was $10\text{ K}\cdot\text{min}^{-1}$ for all experiments. When the setpoint temperature was reached, a CH_4 or $\text{CH}_4\text{-N}_2$ flow was applied. The total duration of this gas flow depended on process conditions. After the desired time on stream had been reached, the CH_4 flow was shut off. Nitrogen kept flushing the system at all times. At this point the heating was gradually decreased to ensure the cooling rate of the reactor did not exceed $10\text{ K}\cdot\text{min}^{-1}$.

After the reactor had cooled down overnight bed samples were retrieved layer-by-layer. This was done by gradual removal of the top most fraction, using a custom made steel tool. Carbon weight fractions were then measured in a LECO A200 carbon analyzer. A tungsten accelerator (LECO, Lecocel –20 40) was added to ensure complete oxidation of the present carbon. Afterwards the remains were discarded.

2.4.2. Reproducibility of experiments

To check reproducibility of measured CH_4 conversion, 10 experiments were performed in duplicate during the research. Average deviation between measured CH_4 conversion was 1.1 percent point, with a maximum of 2.0 percent point, well within the calculated 95% confidence deviation of 3.5 percent point, which was based on the precision

of the CH₄ sensors. For the measured carbon profiles, the calculated 95% confidence deviation was in the order of 0.1%. However, a larger variation was observed (12%) experimentally. This was attributed to the method of retrieving samples from the bed. Since a large axial temperature gradient (up to 10000 K.min⁻¹) was present, a large axial gradient in carbon mass fraction could be expected. In the ideal measurement, the particles in a single sample obtained from the bed have an identical carbon fraction. To be able to meet this uniform fraction the obtained samples have to be significantly smaller than a monolayer of particles removed from the bed. Average sample weight obtained was 1.1 g, corresponding to 4 monolayers.

To obtain a reproducible carbon weight fraction of the obtained samples from the bed, it was found that the sample size fed into the analyzer should be 100 mg at minimum. All carbon measurements were performed in duplo with a sample size between 100 and 150 mg, if enough sample was obtained from the bed. Obtained carbon fractions were taken as average for the layer location of the original bed sample. Obtained carbon profiles were found to be reproducible, results are presented in [appendix A](#). Furthermore, burning off the carbon in pure oxygen at 1100 °C for 6 h yielded a comparable carbon profile, validating the result obtained from the LECO analyzer. Concluding, the resulting errors were caused predominantly by random variations in the experiment and the bed sampling method.

To check the overall H₂ and C balance, both CH₄ and H₂ were measured. To be able to use the TCD signal, no CH₄ could be present in the reactor outflow, therefore it is required to operate at 100% CH₄ conversion. To realize this, an experiment was performed at 1350 °C and a CH₄ residence time of 1.0 s. Furthermore, since the TCD had an upper detection limit of 50% H₂ in N₂ an inlet CH₄ fraction of 0.2 was used. To measure to total carbon deposition, all setup components were weighed before and after the run. The overall carbon and hydrogen balances are presented in [Table 2](#). For this calculation it was assumed that no hydrogen is present in the deposited carbon. The errors denote the calculated absolute percent point errors on the measured value and were based on the errors of the individual components used during each of the measurements.

2.5. Analysis equipment

Particle surface area measurements were performed by gas adsorption measurement (Gemini VII 2390 Surface Area Analyzer, Micrometrics). Trace compound gas measurements were performed using a Varian 450-GC refinery gas analyzer. Methane fractions were measured using MIPEX IR sensors. Hydrogen concentration was measured using a Caldos 5G-Ex TCD. Carbon mass fractions on used particles was measured using a LECO A200 carbon analyzer.

3. Results and discussion

3.1. Carbon deposition measurements in the single particle reactor

Using the single particle reactor, carbon loading over time was measured for several temperatures. For all the data presented in the results section, particle A was used. To measure kinetics, mass and energy transfer limitations should be negligible. Energy and mass transport in the single particle reactor has been discussed in [Section 2.3](#) and [appendix B](#) and was found to not limit the decomposition reaction.

Results are presented in [Fig. 2a](#). Error bars denote the 95%

Table 2
Overall mass balance for C and H measured in the fixed bed at 1350 °C.

	Measured	Expected	Closure	Unit
Carbon	0,803	0,857	94% ±5 pp	g
Hydrogen	30,2	30,5	99% ±7 pp	vol%

confidence interval based on the standard deviation of the measurement mean. With increasing temperature the carbon loading over time increases faster. For the 950 and 1000 °C data, a sigmoid curve is observed. An induction period where carbon is deposited slowly is also observed. A possible explanation for this may be given via a surface activation mechanism, where a nucleus first has to form on the surface before decomposition can occur. After the slow nucleation step the decomposition rate accelerates and carbon is deposited more rapidly. This has been discussed in literature [\[33,31,29\]](#), and shown in experiments comparable to these for short gas residence time systems operating at low CH₄ conversion. This is discussed further in [Section 3.4.1](#).

Additionally, a temperature-dependent maximum loading was observed for the measurements of 1000 °C and up. Near maximum loading the deposition of carbon onto the surface stops or becomes very slow. The likely reason for this has not been established. It was also found that a smooth particle (Si₃N₄, RA surface roughness 12 nm) did not gather a measurable amount of carbon (total mass increase <0.01 mg) after 1 h TOS at 1050 °C. Furthermore, it was found that this maximum loading was reached after a longer time when the methane concentration was lowered via a dilution with nitrogen. In [Appendix A, Fig. A3](#) it is shown that the carbon deposition speed is first order in methane concentration.

To put the measured decomposition rate into perspective, assuming a reactor operating isothermally at 1100 °C, without mass or energy transfer limitations would correspond to a volumetric productivity of 35 mol C.m⁻³.s⁻¹ (1500 kg C.m⁻³.h⁻¹). This assumes a fluidized bed with 50 μm porous particles, and a total available area of 10⁴ m².m⁻³, internal and external area combined. Comparing this productivity to a typical value of 4 mol C.m⁻³.s⁻¹ for methane steam reforming shows that the potential realizable volume based production rate of C and H₂ from methane pyrolysis is high [\[36,37\]](#).

3.2. Carbon deposition and methane conversion

In the previous section, results on carbon deposition were presented under differential conditions, i.e. very low methane conversion. Therefore, no link between methane conversion and carbon deposition could be made. This section reports the data obtained using the fixed bed reactor, providing data of methane conversion, and selectivities towards gaseous hydrocarbons and solid carbon, and solid carbon deposition data as function of both time and location.

For the data presented in [Fig. 3](#) temperature was 1000 °C, particle A was used, gas inlet was 100% CH₄ and the gas residence time was 1.0 s. To measure momentary selectivities towards gaseous intermediates, gas samples were taken using a syringe. The total sample time was in the order of seconds, therefore the gaseous products in the sample syringe reflect the rate towards gaseous intermediates during this period. Via [Eq. 2](#) the momentary selectivity was obtained.

$$S_p = \frac{C_{\text{intermediates}}}{C_{M,\text{in}} - C_{M,\text{out}}} \left[\frac{\text{mol.s}^{-1}}{\text{mol.s}^{-1}} \right] \quad (2)$$

For the selectivity towards solid carbon, carbon profiles were measured at several points in time. Since the bed has to be removed from the reactor and is consumed during carbon analysis in the LECO machine, a total of 4 tests were done, one for each solid selectivity data point. The amount of carbon produced since the previous measurement was then calculated. From this change in amount of carbon, a time-averaged decomposition rate was obtained and used in [Eq. 3](#). This allowed comparison of the selectivities towards gaseous hydrocarbons and solid carbon under the same conditions and at the same time. The momentary selectivity *S* towards phase *p* is defined as:

$$S_p = \frac{\text{production rate of C in phase p}}{\text{total CH}_4\text{conversion rate}} \left[\frac{\text{mol.m}^{-1}.\text{s}^{-1}}{\text{mol.m}^{-1}.\text{s}^{-1}} \right] \quad (3)$$

In [Fig. 3](#) the obtained selectivities and overall CH₄ conversion are

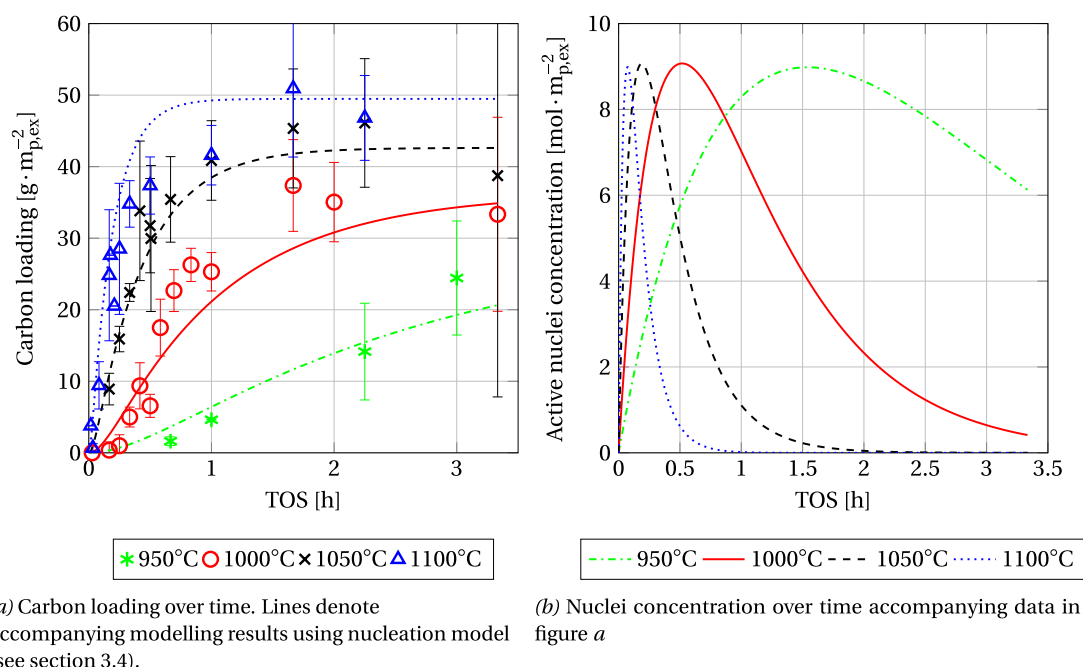


Fig. 2. Experimental carbon loading over time obtained in the single particle reactor and prediction of nucleation kinetics model, various temperatures, particle A.

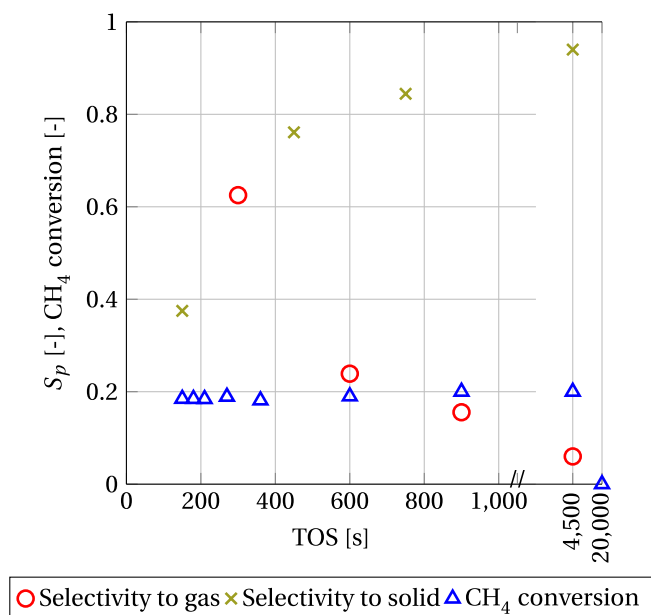


Fig. 3. Methane conversion and momentary selectivity towards gaseous and solid products, measured in a fixed bed at 1000 °C. Gas residence time 1.0 s, Inlet 100% CH_4 , Particle A.

plotted over time.

Methane conversion over time was constant at approximately 0.2 for all but the last ($t = 20,000$ s) measurements. Next to CH_4 and H_2 , the intermediate decomposition products C_2H_4 , C_2H_2 and C_3H_6 were detected. It can therefore be concluded that the conversion of methane towards gaseous intermediates is independent of the induction period observed for carbon deposition, observed in the single particle reactor. In Fig. 4 this is shown conceptually, as function of loading. The rest of the observations discussed in this section are also present in this figure.

The selectivity towards solid carbon increases over time. This is in line with the observed induction period observed for solid carbon deposition. Some solid carbon was found at $t = 300$ s. This result might

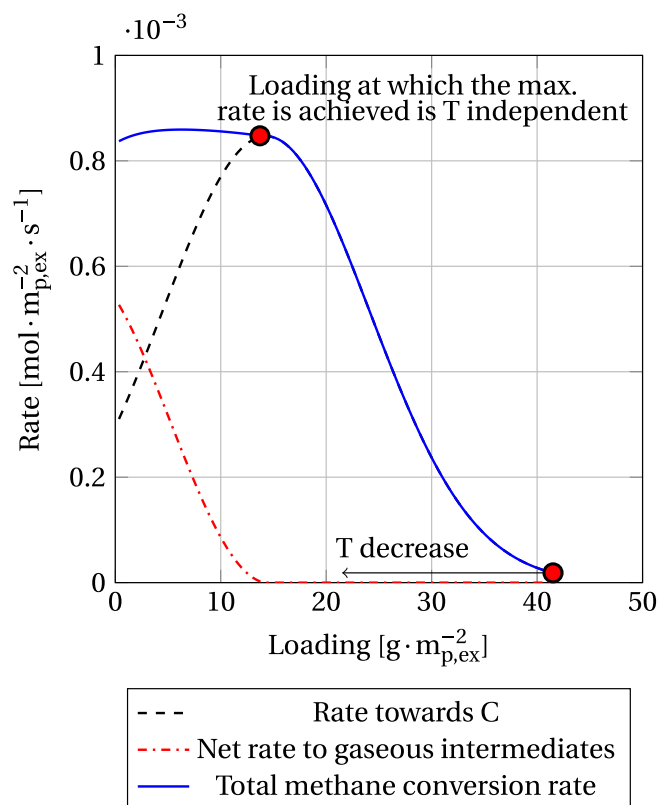


Fig. 4. Methane conversion and carbon deposition rate as function of loading, 1000 °C.

seem to conflict with the single particle results, where no carbon was measured in this initial period. This difference is caused by the detection limits of the used methods. The detection limit for carbon of the LECO used for fixed bed measurements is much lower (equivalent to $0.005 m_{p,ex}^{-2}$) than the carbon loading detectable by the weight difference method used in the single particle experiments (equivalent to $1.2 m_{p,ex}^{-2}$).

$\text{ex})$. The observed loading measured at 300 s in the fixed bed was $0.4 \text{ m}^{-2}_{\text{p,ex}}$.

For the longer TOS the observed fixed bed loadings correspond to the measured single particle loadings. The observed volume fractions of intermediates decreased over time, in line with the increased solid carbon deposition and reduced selectivity to gaseous hydrocarbons. For longer TOS (20000 s), the conversion of methane reduced to effectively 0. The loading at this point corresponds to the maximum loading observed in the single particle reactor, and no carbon was being deposited in the bed at this point. A gas phase measurement confirmed that no methane was being converted to gaseous intermediates at this point, either.

The observation that CH_4 conversion to the first decomposition products, such as ethylene and acetylene, is not related to the induction period observed for carbon deposition implies that methane conversion and carbon deposition are initially, over fresh $\alpha\text{-Al}_2\text{O}_3$, two different processes. At 20000 s however, carbon deposition as well as methane conversion appear to stop almost completely. The only difference between $t = 0$ s and $t = 20000$ s is the amount of carbon deposited on the particles. Therefore, near the maximum loading, the amount of deposited carbon on the available surface does influence the conversion of methane towards gaseous intermediates. Note that the maximum loading is dependent on the temperature and is therefore a function of axial location along the reactor, visualized in Fig. 4.

The observed phenomena are summarized in Fig. 4. The point of maximum loading is temperature dependent, a lower temperature results in a lower maximum carbon loading. The point where the selectivity towards carbon becomes 100% is not known exactly, but appears to occur at a certain carbon loading and appears to be temperature independent.

To further investigate the effect of available surface on the conversion of methane towards gaseous intermediates, the experiment was repeated in a empty tube. Gas residence time and setpoint temperature were kept the same as the original experiment by increasing the CH_4 flow. The total run time was 300 s. CH_4 conversion to gaseous intermediates was 0.2%, only a trace (0.06%vol) of C_2H_4 was detected, this was near the detection limit of the GC. This low CH_4 conversion indicates that the rate of methane conversion is also aided by a surface.

If the desired product is either hydrogen or syngas, from a process development perspective, the production of gaseous intermediates should be minimized. At 1000 °C the gaseous intermediates are mostly formed in the first ± 1000 s, where relatively little carbon is being deposited. After these first 1000 s the production of gaseous intermediates remains low. From Fig. 4, the net production of gaseous intermediates occurs at loadings below $\pm 15 \text{ g} \cdot \text{m}^{-2}_{\text{p,ex}}$. For a process with high carbon efficiency operating at 1000 °C, working below this loading should be avoided. The loading, at which the production of gaseous intermediates stops, appears to be temperature independent. As higher temperatures result in a higher rate, the loading of $\pm 15 \text{ g} \cdot \text{m}^{-2}_{\text{p,ex}}$ is achieved much earlier. In Table 3 the measured selectivities to solid carbon are presented for TOS = 250 s, for various temperature setpoints. Almost no gaseous products were found at these higher temperatures.

Table 3
Measured differential selectivities of methane towards solid carbon at several temperatures, fixed bed, gas residence time 1 s, TOS = 250 s, Particle A.

Setpoint T [°C]	S_{solid} [-]
1300	0.999
1200	0.976
1100	0.967
1000	0.375

3.3. Further fixed bed data

In this section further fixed bed data is presented. Some model results are also incorporated. These model results are discussed in Section 3.5. For all data presented in this section a 50% CH_4 - 50% N_2 inlet was used, gas residence time in the hot zone was 0.6 s, and particle A was used. Conversion over time is presented in Fig. 6. In agreement with Fig. 3 the methane conversion over time is not constant. First, a slight acceleration is observed, thereafter followed by a decrease over time. The decrease and eventual stop of methane conversion is explained by the carbon deposition on the bed, as shown in Section 3.5.

Interestingly, the slight acceleration in overall conversion also means that more intermediates are being formed, as intermediates must be formed before carbon can deposit. This implicates that the initial rate of intermediate formation at $t = 0$ is slower than the intermediate formation rate at maximum methane conversion. A reason for this initially slow intermediates production rate has not been identified. It is speculated that the thermodynamic equilibrium between methane and the intermediates is reached [38], thereby limiting the initial intermediates production rate.

The bed temperature varies significantly over the axial reactor coordinate, therefore the overall CH_4 conversion is a result of decomposition processes at a wide range of temperatures. A temperature and corresponding carbon profile is presented in Fig. 5. Regardless of setpoint temperature used, the first carbon from the inlet side was always found around the point where the local temperature was 850 °C. In Fig. 7 the growth of carbon over time was visualized by measuring three carbon profiles after different runtimes. It is seen here that the growth over time is not linear, as can be expected from the single particle measurements.

In Section 3.5 the model predictions also visible in these figures are discussed.

3.4. Mechanism and modeling

In the experimental data presented earlier, several phenomena are observed to occur during methane pyrolysis for fresh, carbon free $\alpha\text{-Al}_2\text{O}_3$:

1. An initial induction period during which no carbon is deposited.
2. During this period, methane is already being converted to gaseous intermediates.
3. Effects 1 and 2 are most pronounced for temperatures up to 1000 °C. For higher temperatures the deposition starts much earlier and little gaseous intermediates are produced overall.

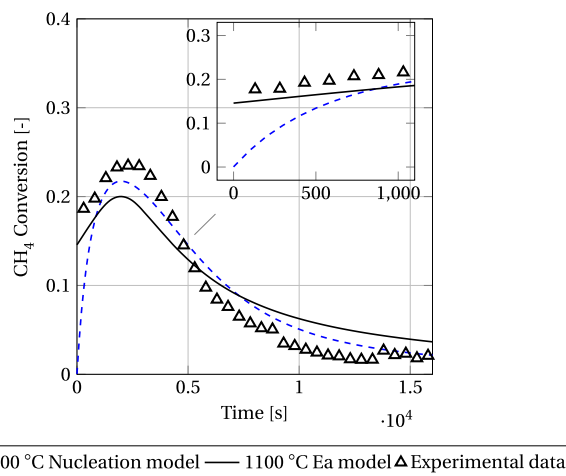


Fig. 6. CH_4 conversion over time measured in fixed bed at 1100 °C, gas residence time 0.6 s, Inlet fraction $\text{CH}_4 = 0.5$, particle A.

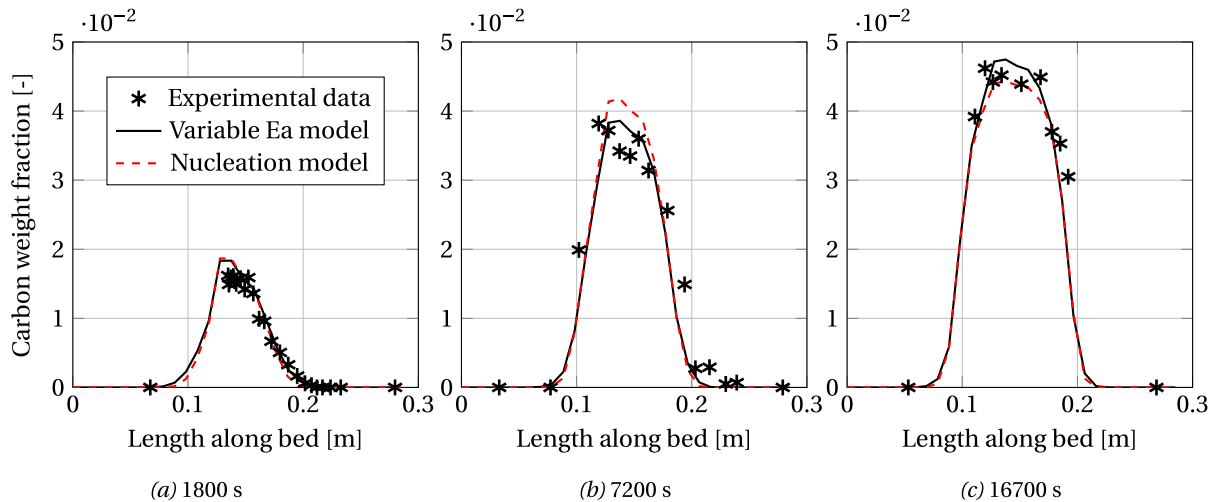


Fig. 7. Carbon profiles in fixed bed measured at different time on stream values, 1100 °C, Gas residence time 0.6 s, Inlet 50%CH₄-50% N₂, Particle A.

4. A temperature dependent maximum carbon loading occurs. When this loading is reached, methane is not converted to solid carbon nor to gaseous intermediates anymore.

All these key phenomena should be incorporated into a model in order to be useful for reactor design and optimization. To predict phenomenon 1, the model needs to have some sort of initiation for carbon deposition. To predict phenomenon 4, the model needs to have a termination mechanism for carbon deposition.

From a process development perspective, the formation of gaseous intermediates should be avoided. The decomposition reactor should be designed so that little gaseous species are produced, for example by increasing the decomposition temperature. Therefore, and for sake of simplicity, phenomenon 2 is not incorporated in either of the models, and gas phase intermediates are not taken into account. This still enables prediction of phenomena 1, 3 and 4 whilst reducing the complexity of the models. Note that this means that this model is not able to make correct predictions for short solids residence time applications, especially for temperatures below 1100 °C.

The first model is a nucleation model based on literature (e.g. [31,32,26,28,23,33]), where a nucleus has to form on the surface in order for carbon to deposit. The second model uses a variable activation energy to describe the acceleration and eventual stop in carbon deposition, using fewer parameters.

3.4.1. Nucleation model

The data presented in the previous sections may be indicative of a nucleation mechanism for carbon deposition. If the formation of this nucleus is the limiting step at low temperature this can explain the

observed acceleration of carbon deposition. After these nuclei are formed the faster carbon deposition reaction becomes dominant and carbon is deposited faster. The published nucleation models do not include a termination mechanism. We included this termination by incorporating a maximum number of nuclei that can be formed and setting the stoichiometry between nuclei and deposited carbon.

The nucleation model takes into account three species: available sites (AS), nuclei (nuc) and deposited carbon (C). In this model, a nucleus can be formed only on an available site. These available sites are consumed when a nucleus forms and are incorporated to limit the number of nuclei that can be formed. Kinetics reported in literature do not limit the growth of nuclei and, by extension, the growth of carbon. It was shown experimentally that the carbon deposition does stop, therefore this addition was made. The conceptual working of the model is presented in Fig. 8.

The amount of available sites (AS) is a particle characteristic, and is temperature dependent. The change from available site to nuclei is described by Eq. 4. It is an exponential decay dependent on temperature and has unit mol.m⁻². This part functions as the initiation to predict phenomenon 1 by an increasing amount of nuclei in the induction period. Additionally, this serves as a brake to limit the amount of carbon that can be deposited. When the amount of available sites is consumed no more carbon can be deposited.

$$R_{AS} = -k_{AS} \exp\left(\frac{-E_{aAS}}{RT}\right) C_{AS} \quad (4)$$

The initial amount of available sites is given by Eq. 5. It does not need to represent a real quantity of a species and can be regarded as a measure for the energy level of the surface. The initial amount of available sites

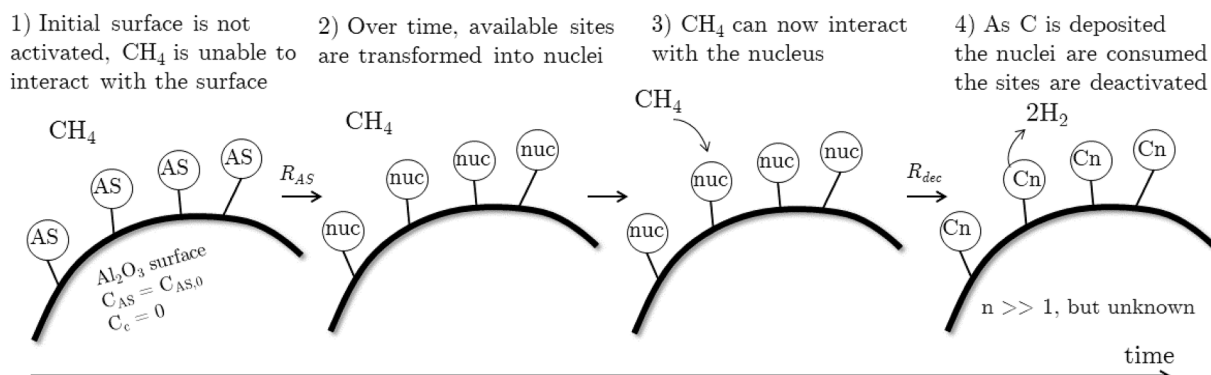


Fig. 8. Nucleation model visualized in steps.

(mol.m⁻²) equals the maximum carbon loading at that temperature. Hence, it causes the carbon deposition to stop.

$$C_{AS,0} = k_{AS,II} \exp\left(\frac{-E_{a,AS,II}}{RT}\right) \quad (5)$$

For nuclei a generation rate and a consumption rate are formulated. Nuclei generation is dependent on the amount of available sites C_{AS} . The nuclei generation rate serves as the initial induction period, and accelerates the carbon deposition in these moments. In this model, it is assumed nuclei do not consume methane. In reality the nuclei likely consists of carbonaceous material, and should therefore originate from methane. This has not been incorporated for simplicity sake: the (molar) mass of a nucleus cannot be measured and was therefore taken as 0. Nuclei consumption is dependent on the carbon deposition rate, it is assumed that every carbon atom deposited consumes a nucleus. Since no data is available on the amount of nuclei present on the surface, it is unknown how much carbon can be deposited per nucleus, for simplicity this stoichiometry was then taken as 1. One could change this stoichiometry to any arbitrary value, provided that the amount of available sites is also changed accordingly. Since the nucleus is removed when a carbon atom is deposited, this model implies the formation of a monolayer of carbon. In reality, this is not possible as the amount of carbon deposited is much larger than one monolayer on the Al₂O₃ surface. Therefore, the real amount of nuclei must be smaller than presented in the model and secondly, more carbon can be deposited per nucleus. The nuclei balance is presented as Eq. 6.

$$R_{nuc} = R_{AS} - R_{dec} = k_{AS} \exp\left(\frac{-E_{a,AS}}{RT}\right) C_{AS} - C_M C_{nuc} k_{dec} \exp\left(\frac{-E_{a,dec}}{RT}\right) \quad (6)$$

For the carbon deposition, from experimental results it is known that the decomposition rate is first order in available area (Tables 8 and 9 in appendix A). Furthermore, it is shown that the carbon deposition rate is first order in methane pressure (Fig. A.3 in appendix A). From Section 3.2 it is known that for the first steps in the decomposition mechanism towards gaseous intermediates, no nuclei are required. As stated before, the gaseous intermediates are not taken into account. It is assumed that the total methane reaction rate is dependent on the nuclei concentration. Although this is not correct in the initiation period. This will only negatively affect predictions in the initial periods for temperatures below 1000 °C. This is incorporated in Eq. 7:

$$R_{dec} = C_M C_{nuc} k_{dec} \exp\left(\frac{-E_{a,dec}}{RT}\right) \quad (7)$$

The equations mentioned above were fitted to the experimental data presented in Fig. 2a by minimizing the difference between model and experimental values in MATLAB using the fmincon, fminunc and nlinfit routines. Eq. 8 was used for the minimalization of the error σ for j datasets of temperature T_j consisting of N datapoints, with C being the model or experimental carbon loading:

$$\sigma = \sum_{T=T_1}^{T_j} \sum_{i=1}^{N_j} \frac{1}{N_j} (C_{mod,j,i} - C_{exp,j,i})^2 \quad (8)$$

In Fig. 2a model results are presented. Modeled loading over time approximates experimental values. The sigmoid curves are observed for the lower 2 temperatures. The initial slow deposition of carbon is explained by the lack of nuclei, which are presented in Fig. 2b. At lower temperatures the nuclei generation rate (Eq. 4) is relatively slow. The sigmoid curve is therefore most visible at lower temperatures. At higher runtime and higher loadings the number of available sites approaches zero (Fig. A.4 in appendix A). From Fig. 2b and Eq. 6 this is seen as the decrease in available nuclei eventually leading to a stop in carbon deposition.

Parameter values are presented in Table 4. Errors present 95% confidence intervals. The rate constant does not accurately represent the turnover frequency of the hydrocarbons on the Al₂O₃ surface. The

Table 4

Kinetic parameters.

	Ea [kJ.mol ⁻¹]	Error Ea [kJ.mol ⁻¹]	k	Error k	unit k
Dec	324	±1,42·10 ⁸	±4.8·10 ⁶	m _g .mol ⁻¹ .s ⁻¹	
AC	243	±3	3.45·10 ⁶	±2.4·10 ⁴	s ⁻¹
AC ₀	45	±4	2,54·10 ⁴	±2.0·10 ²	mol.m _p ⁻² .s ⁻¹

relevant component in Eq. 7 is taken as methane since this concentration is known. In reality this will most likely be some larger hydrocarbon formed as an intermediate during methane decomposition. Since this intermediate will be present in a lower concentration the true turnover frequency will be higher. Methane is used in the equation as the concentration of this component is known and secondly because the concentration of the relevant intermediate reactant(s) will be directly proportional to the CH₄ concentration.

Correlation coefficients were calculated to range from 0.93 to 1 across all parameters. This strong cross-correlation can be expected because available sites and nuclei concentration could not be measured.

It is known that the particle surface has a (or multiple) characteristic (s) that influence the carbon deposition rate. All kinetic data here were obtained using particle A, however experiments with a smooth (RA surface roughness 12 nm) resulted in no deposited carbon after 1 h at 1050 °C. Therefore the parameters presented here need to be determined for each particle type.

3.4.2. Variable activation energy model

Variable activation energy models are used to describe a large set of parallel and consecutive reactions [39–42]. The effect of the complex reaction network is lumped in the variable activation energy. In this work, the variable activation energy uses a change in activation energy to describe the observed acceleration and eventual stop of carbon deposition. As is the case with the nucleation model presented in the previous section, methane is taken to be the reactive molecule. In reality this will be an intermediary larger molecule. The formation of this intermediary molecule is not taken into account.

The model workings are visualized in Fig. 9. It is assumed that the deposition of the first carbon is relatively slow. This is comparable to the formation of the nucleus of the first model and is incorporated via a relatively high activation energy. When the initial carbon has been deposited it becomes easier to deposit additional carbon. This translates to a lower activation energy. With further increasing carbon loading the activation energy increases again. The activation energy as function of carbon loading will therefore have a parabolic shape, as visualized conceptually in Fig. 9.

The use of a variable activation energy in kinetics is seen by some as indicative of an overly simplistic or overall incorrect kinetics approach [40,42,41]. In this work, no detailed fundamental study into the decomposition steps has been performed, nor was it aimed to do so. We merely evaluated if such a model could describe experimental results. A variable activation energy cannot be regarded as an activation energy in the fundamental sense, but is a result of an interplay between several simultaneously occurring reaction steps or processes [39–42]. For methane pyrolysis, the reaction network is simplified in the sense that several intermediate species are not regarded.

The carbon deposition is described by Eq. 9. The parameter k_{dec} incorporates the particle dependent characteristic of the amount of available sites. Therefore, only a single equation is needed. The activation energy is a function of carbon loading and is described by Eq. 10.

$$\frac{dC_c}{dt} = R_{dec} = C_M k_{dec} \exp\left(\frac{-E_{a,dec}}{RT}\right) \quad (9)$$

$$E_{a,dec} = p_2 \cdot C_c^2 + p_1 \cdot C_c + p_0 [\text{J.mol}^{-1}] \quad (10)$$

First step: $\text{CH}_4 \rightarrow \text{C}_n$ 0) Some intermediate C_n is formed, size is unknown, $P_{\text{C}_n} \triangleq P_{\text{CH}_4}$, $\rightarrow \text{CH}_4$ is incorporated in rates

Step is not taken into account in the model

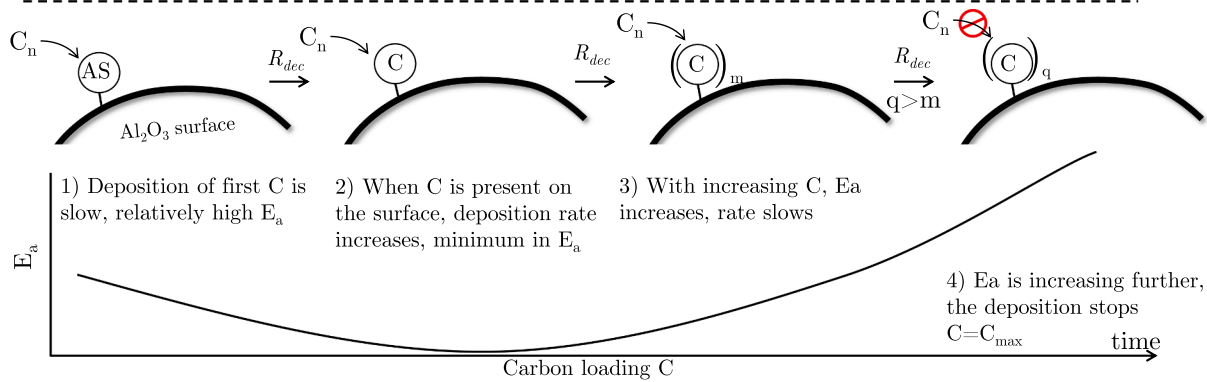


Fig. 9. Variable activation energy model visualized in steps.

Combination of Eq. 9 and 10 yields:

$$\frac{dC_c}{dt} = C_M k_{dec} \exp\left(\frac{-(p_2 \cdot C_c^2 + p_1 \cdot C_c + p_0)}{RT}\right) \quad (11)$$

Which has the analytical solution:

$$k_{dec} C_M t = \frac{\sqrt{\pi RT} \exp\left(\frac{p_2^2 - 4p_0 p_1}{4p_2 RT}\right) \left(\operatorname{erfi}\left[\frac{p_1 + 2p_2 C_c}{2\sqrt{p_2 RT}}\right] - \operatorname{erfi}\left[\frac{p_1}{2\sqrt{p_2 RT}}\right] \right)}{2\sqrt{p_2}} \quad (12)$$

Eq. 12 was used to calculate loading over time. The fitting routine was the same as the first model, using Eq. 8 describing the error. Fit parameters were k_{dec} and the 3 polynomial coefficients. The obtained fit is presented in Fig. 10. The corresponding activation energy as function of carbon loading is presented in Fig. 12.

After parameterization this model describes the experimental data. The sigmoid curves are present in the modeled loading. For all temperatures, the deposition speed has reached a maximum at $C_c = 15$

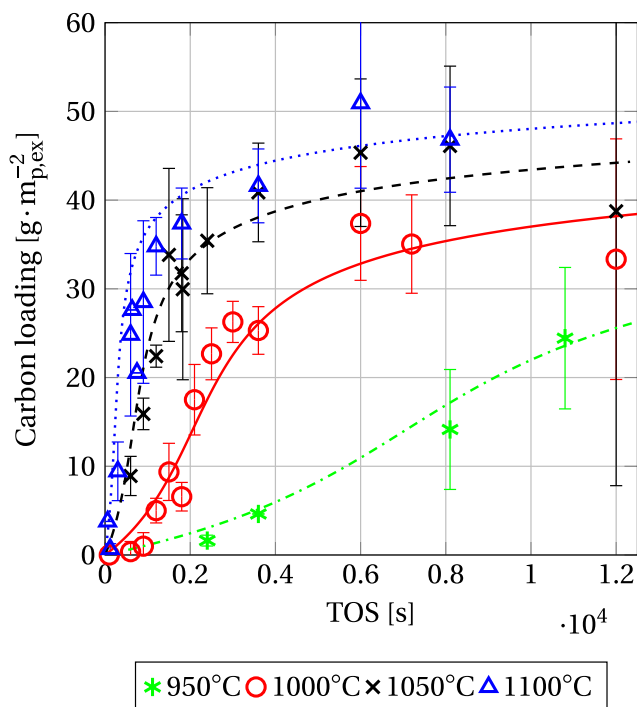


Fig. 10. Carbon loading over time in the single particle reactor with activation energy distribution results, several temperatures, particle A.

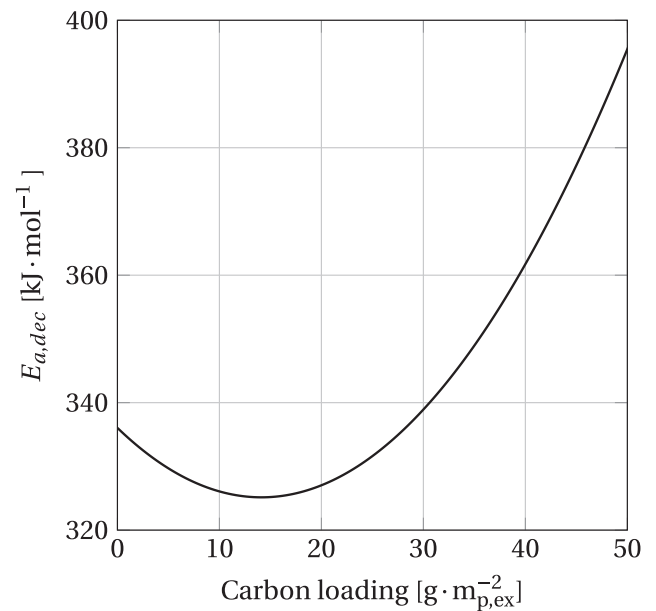


Fig. 12. Fitted activation energy as function of carbon loading, corresponding to the results in Fig. 10.

$m_{p,ex}^{-2}$, being the inflection point in the sigmoid curve and the minimum of the E_a parabola.

In Table 5 the fitted parameters are presented. Calculated correlation coefficients indicate a strong (0.9–1) cross correlation between all the polynomial parameters, but not between the polynomial parameters and the rate constant (0–0.3). see Fig. 11.

As is the case with the nucleation model, these parameter values are only valid for particle A. An adaption of these parameters needs to be made for usage of other particles.

Table 5
Fitted parameters for activation energy distribution model.

	Value	Error	Unit
k_{dec}	$1,97 \cdot 10^9$	$6,7 \cdot 10^6$	$\text{m}_g^3 \cdot \text{m}_p^{-2} \cdot \text{s}^{-1}$
p_0	$3,3 \cdot 10^5$	$6,3 \cdot 10^2$	$\text{J} \cdot \text{mol}^{-1}$
p_1	$-18,5 \cdot 10^3$	$3,6 \cdot 10^2$	$\text{J} \cdot \text{m}^2 \cdot \text{mol}^{-2}$
p_2	$7,9 \cdot 10^3$	64	$\text{J} \cdot \text{m}^4 \cdot \text{mol}^{-3}$

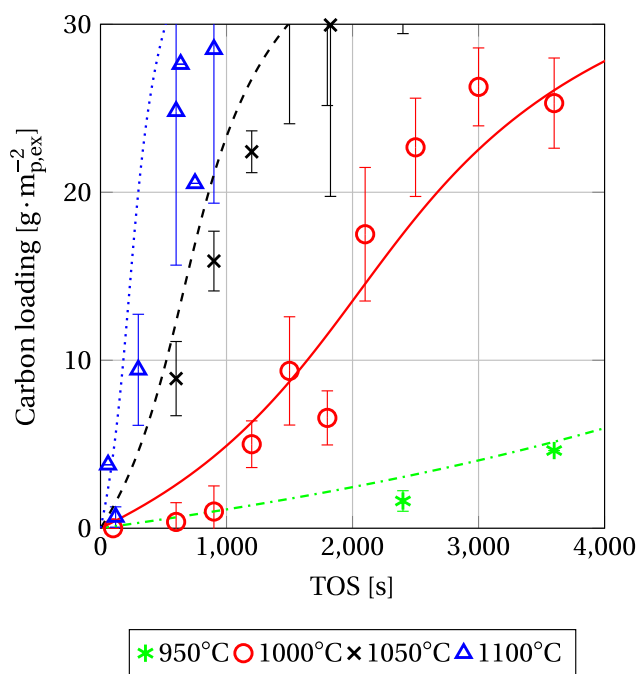


Fig. 11. Carbon loading over time in the single particle reactor with activation energy distribution results, several temperatures, particle A. Zoomed in from Fig. 10.

3.4.3. Comparing both models

Comparing both models, the overall accuracy of the fit, as measured by Eq. 8, is slightly better for the first model (total deviation over all datapoints $418 \text{ m}^{-2}_{\text{p,ex}}$ for model 1 versus $477 \text{ m}^{-2}_{\text{p,ex}}$ for model 2). The accuracy for both models is comparable to the error estimates on the experimental data (summing to $405 \text{ m}^{-2}_{\text{p,ex}}$), and it is argued that both models predict the experimental loading with comparable accuracy. However, there are a few other aspects that vary between both models. The first model uses more parameters (6 vs. 4), which (as a result) have a higher cross correlation. For a process design it is mainly desired to describe carbon deposition, which both models are able to do.

3.5. Verification of kinetics in a fixed bed

In this work a fixed bed was chosen because it is a relatively simple system that could be evaluated without changes to the used setup. From a process development perspective there are numerous other reactors that may be more suitable for this process, as well as the option of porous particles. This will be evaluated in a separate publication.

In this section fixed bed results are compared to model predictions 3.4. Both the kinetics were incorporated in a fixed bed model. In this model it is assumed that the total methane conversion rate is equal to the carbon deposition rate, meaning that the net formation of intermediates is not taken into account, as discussed earlier. In the fixed bed model, the measured axial temperature profiles were used as input and were taken as constant over time. More details on the model and the differential equations describing this system are presented in appendix D. The bed temperature varies significantly over the axial reactor coordinate, therefore the overall CH_4 conversion is a result of decomposition processes at a wide range of temperatures. The induction period will play a role for temperatures below $\pm 1050^\circ\text{C}$.

The model prediction for CH_4 conversion over time is in reasonable agreement with the experimental results. For the nucleation model the predicted conversion at $t = 0$, is 0. This is because no available sites have been transformed into nuclei at this point. Even though accurate measurement of CH_4 conversion in the first $\pm 100 \text{ s}$ is complicated because the remaining nitrogen is still being flushed out by the newly

introduced methane, it is clear that some methane is already being converted. In Section 3.2 this is also described. For the variable activation energy model this difference is not present as the initial reaction rate is nonzero for these kinetics.

A large part of the bed has a lower temperature than the setpoint temperature, however the carbon deposition is slow here. The lower temperature areas of the bed do not contribute significantly to the total carbon deposition. A test was carried out with a setpoint of 1000°C . Here, the production of gaseous intermediates becomes much more relevant. The required loading of $\pm 15 \text{ g}\cdot\text{m}^{-2}_{\text{p,ex}}$ takes significantly longer to reach, see Fig. A.7. Neither of the models is able to accurately predict methane conversion for this temperature, evident from Fig. A.7 in appendix A. Concluding, at lower temperatures the production of gaseous intermediates is much more pronounced and for accurate methane conversion predictions, should be taken into account. At 1100°C and above, this is not the case.

In Fig. 7 the measured and predicted carbon profiles are presented for three different total runtimes, so that the growth of the carbon profile is visible. The experimental results show that the growth over time is not linear, as can be expected from the single particle results and the total CH_4 conversion over time. For all three run times the predictions of both models are in good agreement with the experimental results. Both kinetic models therefore accurately predict when, and where carbon is deposited. This, and the prediction of CH_4 conversion over time provides confidence that the kinetics obtained in the single particle reactor can be used to predict CH_4 conversion and carbon deposition in a fixed bed. Hence, the kinetics can be used as a rational basis for reactor design and process development.

4. Conclusions

This work describes a first attempt to quantitatively describe carbon deposition from methane pyrolysis on nonporous particles in a way useful for reactor design and process development. A method was developed to characterize carbon deposition on a specific single particle. Using this method, an accurate prediction of the carbon deposition behavior of many particles in a fixed bed was possible.

Detailed data on carbon deposition as function of time and temperature is reported. It was found that carbon deposition accelerates in the first moments after first contacting with methane. Additionally, a maximum carbon loading was found on the used nonporous particles. For 1000°C , it was shown that even though carbon deposition does not occur directly after first contacting with methane, methane is being converted to gaseous intermediates. Over time, as carbon deposition starts and accelerates, the selectivity to gaseous intermediates greatly reduces. This effect is most pronounced at temperatures below 1100°C . For a hydrogen or syngas production process the formation of gaseous hydrocarbons should be avoided, therefore a sufficiently high temperature and solids residence time in the decomposition reactor is required so that the net production of intermediates is largely avoided.

Two types of kinetic models were presented. In neither of these models, the gaseous intermediates were included. Both models accurately predict carbon deposition and methane conversion at 1100°C over time in a fixed bed system. Therefore, for a decomposition reactor operating at 1100°C it is sufficient to only describe the solid deposition to accurately describe methane conversion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors wish to gratefully acknowledge several people. Benno,

Johan and Ronald for their invaluable help during the design, construction and troubleshooting of the setup. Ronald Schoonebeek and Jan Veerman for their valuable suggestions. Norpro Saint Gobain for supplying the first batch of ceramic carrier material.

This work was supported financially by Shell Global Solutions International.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cej.2021.130412>.

References

- [1] J. Meckling, T. Sterner, G. Wagner, Policy sequencing toward decarbonization, *Nature Energy* 2 (12) (2017) 918–922, <https://doi.org/10.1038/s41560-017-0025-8>.
- [2] A. Holmen, O.A. Rokstad, A. Solbakken, High-Temperature Pyrolysis of Hydrocarbons. 2. Naphtha to Acetylene, *Industrial and Engineering Chemistry Process Design and Development* 18 (4) (1979) 653–657. doi:10.1021/i260072a014.
- [3] L. Han, T.K. Lim, Y.J. Kim, H.S. Hahm, M.S. Kim, Hydrogen production by catalytic decomposition of methane over carbon nanofibers, *Mater. Sci. Forum* 510–511 (2) (2006) 30–33, <https://doi.org/10.4028/0-87849-995-4.30>.
- [4] V.V. Chesnokov, A.S. Chichkan, 1-s2.0-S036031990900144X-main.pdf, international journal of hydrogen energy 34 (7) (2009) 2979–2985.
- [5] N. Rahimi, D. Kang, J. Gelinas, A. Menon, M.J. Gordon, H. Metiu, E.W. McFarland, Solid carbon production and recovery from high temperature methane pyrolysis in bubble columns containing molten metals and molten salts, *Carbon* 151 (2019) 181–191, <https://doi.org/10.1016/j.carbon.2019.05.041>.
- [6] A.C. Lua, H.Y. Wang, Hydrogen production by catalytic decomposition of methane over Ni-Cu-Co alloy particles, *Appl. Catal. B: Environ.* 156–157 (6) (2014) 84–93, <https://doi.org/10.1016/j.apcatb.2014.02.046>.
- [7] S. Schneider, S. Bajohr, F. Graf, T. Kolb, State of the Art of Hydrogen Production via Pyrolysis of Natural Gas, *ChemBioEng Rev.* 7 (5) (2020) 150–158, <https://doi.org/10.1002/cben.202000014>.
- [8] R. Aiello, J.E. Fiscus, H.C. Zur Loye, M.D. Amiridis, Hydrogen production via the direct cracking of methane over Ni/SiO₂: Catalyst deactivation and regeneration, *Applied Catalysis A: General* 192 (2) (2000) 227–234. doi:10.1016/S0926-860X(99)00345-2.
- [9] I. Suelves, M.J. Lázaro, R. Moliner, B.M. Corbella, J.M. Palacios, Hydrogen production by thermo catalytic decomposition of methane on Ni-based catalysts: Influence of operating conditions on catalyst deactivation and carbon characteristics, *Int. J. Hydrogen Energy* 30 (15) (2005) 1555–1567, <https://doi.org/10.1016/j.ijhydene.2004.10.006>.
- [10] M.A. Ermakova, D.Y. Ermakov, G.G. Kuvshinov, Effective catalysts for direct cracking of methane to produce hydrogen and filamentous carbon. Part I. Nickel catalysts, *Applied Catalysis A: General* 201 (1) (2000) 61–70. doi:10.1016/S0926-860X(00)00433-6.
- [11] N.Z. Muradov, CO₂-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel, *Energy Fuels* 12 (1) (1998) 41–48, <https://doi.org/10.1021/ef9701145>.
- [12] N. Muradov, F. Smith, A. T-Raissi, Catalytic activity of carbons for methane decomposition reaction, *Catalysis Today* 102–103 (2005) 225–233, <https://doi.org/10.1016/j.cattod.2005.02.018>.
- [13] N. Muradov, Catalysis of methane decomposition over elemental carbon, *Catal. Commun.* 2 (3–4) (2001) 89–94, [https://doi.org/10.1016/S1566-7367\(01\)00013-9](https://doi.org/10.1016/S1566-7367(01)00013-9).
- [14] J. Ashok, S.N. Kumar, A. Venugopal, V.D. Kumari, S. Tripathi, M. Subrahmanyam, CO_x free hydrogen by methane decomposition over activated carbons, *Catal. Commun.* 9 (1) (2008) 164–169, <https://doi.org/10.1016/j.catcom.2007.05.046>.
- [15] Z. Bai, H. Chen, B. Li, W. Li, Catalytic decomposition of methane over activated carbon, *J. Anal. Appl. Pyrol.* 73 (2) (2005) 335–341, <https://doi.org/10.1016/j.jaap.2005.03.004>.
- [16] A. Abánades, E. Ruiz, E.M. Ferruelo, F. Hernández, A. Cabanillas, J.M. Martínez-Val, J.A. Rubio, C. López, R. Gavela, G. Barrera, C. Rubbia, D. Salmieri, E. Rodilla, D. Gutiérrez, Experimental analysis of direct thermal methane cracking, *Int. J. Hydrogen Energy* 36 (20) (2011) 12877–12886, <https://doi.org/10.1016/j.ijhydene.2011.07.081>.
- [17] R. Moliner, I. Suelves, M.J. Lázaro, O. Moreno, Thermocatalytic decomposition of methane over activated carbons: influence of textural properties and surface chemistry, *Int. J. Hydrogen Energy* 30 (3) (2005) 293–300.
- [18] A. Holmen, Direct conversion of methane to fuels and chemicals, *Catal. Today* 142 (1–2) (2009) 2–8, <https://doi.org/10.1016/j.cattod.2009.01.004>.
- [19] S. Rodat, S. Abanades, J. Coulié, G. Flamant, Kinetic modelling of methane decomposition in a tubular solar reactor, *Chem. Eng. J.* 146 (1) (2009) 120–127, <https://doi.org/10.1016/j.cej.2008.09.008>.
- [20] D.M. Matheu, A.M. Dean, J.M. Grenda, W.H. Green, Mechanism generation with integrated pressure dependence: A new model for methane pyrolysis, *J. Phys. Chem. A* 107 (41) (2003) 8552–8565, <https://doi.org/10.1021/jp0345957>.
- [21] A. Vasilou, M. Nimlos, G.B. Ellison, Mechanism of the thermal decomposition of furan, in: ACS National Meeting Book of Abstracts, ACS Publications, 2009.
- [22] A.M. Dunker, S. Kumar, P.A. Mulawa, Production of hydrogen by thermal decomposition of methane in a fluidized-bed reactor - Effects of catalyst, temperature, and residence time, *Int. J. Hydrogen Energy* 31 (4) (2006) 473–484, <https://doi.org/10.1016/j.ijhydene.2005.04.023>.
- [23] P. Harris, Chemistry and physics of carbon, *Mater. Sci. Technol.* 13 (12) (1997) 1066, <https://doi.org/10.1179/mst.1997.13.12.1066>.
- [24] B. Eisenberg, H. Bliss, Kinetics of methane pyrolysis, in: *Chem. Eng. Prog. Symp. Ser.*, Vol. 63, Yale Univ., New Haven, CT, 1967, pp. 3–17. URL: http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=5142124.
- [25] G.H. Denis, T.E. Daubert, Application of quasilinearization to methane pyrolysis, *AIChE J.* 20 (4) (1974) 720–727, <https://doi.org/10.1002/aic.690200413>.
- [26] H.B. Palmer, J. Lahaye, K.C. Hou, On the kinetics and mechanism of the thermal decomposition of methane in a flow system, *J. Phys. Chem.* 72 (1) (1968) 348–353, <https://doi.org/10.1021/j100847a068>.
- [27] J.L. Pinilla, I. Suelves, M.J. Lázaro, R. Moliner, Kinetic study of the thermal decomposition of methane using carbonaceous catalysts, *Chem. Eng. J.* 138 (1–3) (2008) 301–306, <https://doi.org/10.1016/j.cej.2007.05.056>.
- [28] K.I. Makarov, V.K. Pechik, Kinetics of methane pyrolysis under conditions of pyrolytic carbon formation, *Carbon* 12 (4) (1974) 391–403, [https://doi.org/10.1016/0008-6223\(74\)90004-9](https://doi.org/10.1016/0008-6223(74)90004-9).
- [29] K.I. Makarov, V.K. Pechik, Kinetics of methane thermal decomposition on the carbon surface in transient regime, *Carbon* 7 (2) (1969) 279–285, [https://doi.org/10.1016/0008-6223\(69\)90110-9](https://doi.org/10.1016/0008-6223(69)90110-9).
- [30] J. Lahaye, G. Prado, J.B. Donnet, Nucleation and growth of carbon black particles during thermal decomposition of benzene, *Carbon* 12 (1) (1974) 27–35, [https://doi.org/10.1016/0008-6223\(74\)90037-2](https://doi.org/10.1016/0008-6223(74)90037-2).
- [31] D.V. Fedoseev, S.P. Vnukov, B.V. Derjaguin, Physico-chemical theory of graphite growth from hydrocarbons, *Carbon* 17 (6) (1979) 453–458, [https://doi.org/10.1016/0008-6223\(79\)90033-2](https://doi.org/10.1016/0008-6223(79)90033-2).
- [32] A.E. Witt, A preliminary investigation of the formation of carbon black by the pyrolysis of residual fuel oil fe 2 112S IBARs State University, Ph.D. thesis, Massachusetts Institute of Technology (1966).
- [33] P.A. Tesner, T.D. Smegiriova, V.G. Knorre, Kinetics of dispersed carbon formation, *Combust. Flame* 17 (2) (1971) 253–260, [https://doi.org/10.1016/S0010-2180\(71\)80168-2](https://doi.org/10.1016/S0010-2180(71)80168-2).
- [34] L.C. Blackman, G. Saunders, A.R. Ubbelohde, Defect structure and properties of pyrolytic carbons, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 264 (1316) (1961) 19–40. doi:10.1098/rspa.1961.0183.
- [35] P. Sander, U. Kaiser, M. Altebockwinkel, L. Wiedmann, A. Benninghoven, R.E. Sah, P. Koidl, Depth profile analysis of hydrogenated carbon layers on silicon by x-ray photoelectron spectroscopy, auger electron spectroscopy, electron energy-loss spectroscopy, and secondary ion mass spectrometry, *J. Vacuum Sci. Technol. A: Vacuum, Surfaces, Films* 5 (4) (1987) 1470–1473.
- [36] M. Zafir, A. Gavrilidis, Catalytic combustion assisted SMR in a plate reactor, *Chem. Eng. Sci.* 58 (17) (2003) 3947–3960.
- [37] J.A. Moulijn, M. Makkee, A.E. Van Diepen, *Chemical process technology*, Vol. 51, John Wiley & Sons, 2013. doi:10.5860/choice.51-2107.
- [38] C. Guéret, M. Daroux, F. Billaud, Methane pyrolysis: Thermodynamics, *Chem. Eng. Sci.* 52 (5) (1997) 815–827, [https://doi.org/10.1016/S0009-2509\(96\)00444-7](https://doi.org/10.1016/S0009-2509(96)00444-7).
- [39] S. Vyazovkin, Reply to What is meant by the term variable activation energy when applied in the kinetics analyses of solid state decompositions (crystallization reactions)? *Thermochim. Acta* 397 (1–2) (2003) 269–271, [https://doi.org/10.1016/S0040-6031\(02\)00391-X](https://doi.org/10.1016/S0040-6031(02)00391-X).
- [40] A.K. Galwey, What is meant by the term 'variable activation energy' when applied in the kinetic analyses of solid state decompositions (crystallization reactions)? *Thermochimica acta* 397 (1–2) (2003) 249–268.
- [41] S. Vyazovkin, On the phenomenon of variable activation energy for condensed phase reactions, *New J. Chem.* 24 (11) (2000) 913–917, <https://doi.org/10.1039/b004279j>.
- [42] F.H. Constable, The mechanism of catalytic decomposition, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 108 (746) (1925) 355–378. doi:10.1021/ie50602a034.
- [43] F. Geiger, C.A. Busse, R.I. Loehrke, The vapor pressure of indium, silver, gallium, copper, tin, and gold between 0.1 and 3.0 bar, *Int J Thermophys* 8 (4) (1987) 425–436, <https://doi.org/10.1007/BF00567103>.