Methane decomposition kinetics on unfunctionalized alumina surfaces

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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:

\[ CH₄ → C + 2H₂ \quad ΔH_r = +75.6kJmol⁻¹ \quad 298K \]  (1)

Deposition of solid carbon 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 → C₂H₂ → C₂H₄ → 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
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 \( \alpha \)-Al\(_2\)O\(_3\). 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 \( \alpha \)-alumina particles were used in this work. Particle A (1.5 mm diameter, 99% Al\(_2\)O\(_3\), \( \rho_p = 3740\) kg.m\(^{-3}\)) was obtained from Saint-Gobain NorPro. Particle B (3 mm diameter, 99% Al\(_2\)O\(_3\), \( \rho_p = 3688\) kg.m\(^{-3}\)) was obtained from Baan Machines. Si\(_3\)N\(_4\) 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%H\(_2\)) 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, SuperKantal A1, Salomons Metalen) wrapped around a cylindrical radiation element (99.7% Al\(_2\)O\(_3\), 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 Al\(_2\)O\(_3\) particle was suspended in a \( \text{CH}_4 \) flow by placing it in a conical reactor. A reactor tube (11 mm ID, 99.9% Al\(_2\)O\(_3\), Haldewanger) was placed inside the oven. The conical Al\(_2\)O\(_3\) 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 placed inside the oven 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
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, and shows that the particle temperature does not deviate from the setpoint temperature significantly. Hence, the decomposition reaction is not heat transfer limited.

With the cone present in the reactor tube the system was heated to setpoint (Heating rate 10 K.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 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 mol.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 K.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 \( \text{Al}_2\text{O}_3 \) tube and was collected in a 5 ml sample glass connected to the reactor. The particle cooled down in \( \pm 1 \) 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 consisted 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 \( \text{CH}_4 \) 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 \( \text{Al}_2\text{O}_3 \) 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 those datapoints were not included in the final dataset.

Inflowing gas was \( \text{CH}_4 \) and \( \text{N}_2 \) with flow rates ranging from 0–100 Nml.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) \( \text{Al}_2\text{O}_3 \) inserts were placed in the reactor, decreasing dead volume outside 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 \( \text{Al}_2\text{O}_3 \) tube and was collected in a 5 ml sample glass connected to the reactor. The particle cooled down in \( \pm 1 \) 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.

#### Table 1

| Run number | Measured loading [g.m\(^{-2}\)p.e.] |
|------------|-------------------------------------|
| 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 Nml.min\(^{-1}\) \( \text{N}_2 \) flow during heating and cooling of the reactor.

The heating rate was 10 K.min\(^{-1}\) for all experiments. When the setpoint temperature was reached, a \( \text{CH}_4 \) or \( \text{CH}_2\text{N}_2 \) flow was applied. The total duration of this gas flow depended on process conditions. After the desired time on stream had been reached, the \( \text{CH}_4 \) 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 K.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 \( \text{CH}_4 \) conversion, 10 experiments were performed in duplicate during the research. Average deviation between measured \( \text{CH}_4 \) 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 CH$_4$ 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 $^\circ$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 H$_2$ and C balance, both CH$_4$ and H$_2$ were measured. To be able to use the TCD signal, no CH$_4$ could be present in the reactor outflow, therefore it is required to operate at 100% CH$_4$ conversion. To realize this, an experiment was performed at 1350 $^\circ$C and a CH$_4$ residence time of 1.0 s. Furthermore, since the TCD had an upper detection limit of 50% H$_2$ in N$_2$ an inlet CH$_4$ 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% 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 $^\circ$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 CH$_4$ conversion. This is discussed further in Section 3.4.1.

Additionally, a temperature-dependent maximum loading was observed for the measurements of 1000 $^\circ$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 (Si$_3$N$_4$, 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 $^\circ$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 $^\circ$C, without mass or energy transfer limitations would correspond to a volumetric productivity of 35 mol C.m$_{-2}$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 $10^4$ m$^2$.m$^{-3}$, internal and external area combined. Comparing this productivity to a typical value of 4 mol C.m$_{-2}$s$^{-1}$ for methane steam reforming shows that the potential realizable volume based production rate of C and H$_2$ 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 $^\circ$C, particle A was used, gas inlet was 100% CH$_4$ 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.

$$S_p = \frac{C_{intermediates}}{C_{in} - C_{out}} \cdot \frac{mol \cdot s^{-1}}{mol \cdot s^{-1}}$$

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:

$$S_p = \frac{production \ rate \ of \ C \ in \ phase \ p}{total \ CH_4 conversion \ rate} \cdot \frac{mol \cdot m^{-2} \cdot s^{-1}}{mol \cdot m^{-2} \cdot s^{-1}}$$

In Fig. 3 the obtained selectivities and overall CH$_4$ conversion are
Methane conversion over time was constant at approximately 0.2 for all but the last ($t = 20000$ s) measurements. Next to CH$_4$ and H$_2$, the intermediate decomposition products C$_2$H$_4$, C$_2$H$_2$ and C$_3$H$_6$ 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 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$^2$ p.ex.) than the carbon loading detectable by the weight difference method used in the single particle experiments (equivalent to 1.2 m$^2$ p.)
temperatures, fixed bed, gas residence time 1 s, TOS
Measured differential selectivities of methane towards solid carbon at several
Table 3
| Setpoint T [°C] | $S_{\text{solid}}$ [-] |
|-----------------|-------------------------|
| 1300            | 0.990                   |
| 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
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 forma-
tion rate at maximum methane conversion. A reason for this initially
slow intermediates production rate has not been identified. It is specu-
lated 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 co-
dordinate, therefore the overall CH$_4$ conversion is a result of decompo-
sition processes at a wide range of temperatures. A temperature and
corresponding carbon profile is presented in Fig. 5. Regardless of set-
point 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
$\alpha$-Al$_2$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 resi-
dence time 0.6 s, Inlet fraction CH$_4$ = 0.5, particle A.](image-url)
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.

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

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

\[ C_{AS,0} = k_{AS,0} \exp \left( -\frac{E_{AS,0}}{RT} \right) \]  

(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 nuclei, 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 \(\text{Al}_2\text{O}_3\) surface. Therefore, the real amount of nuclei must be smaller than presented in the model and secondly, more carbon can be deposited per nuclei. The nuclei balance is presented as Eq. 6.

\[ R_{dec} = R_{AS} - R_{dep} = k_{AS,0} \exp \left( -\frac{E_{AS,0}}{RT} \right) C_{AS} - C_{M} C_{\text{mon}} k_{\text{dec}} \exp \left( -\frac{E_{\text{dec}}}{RT} \right) \]  

(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:

\[ R_{dep} = C_{M} C_{\text{mon}} k_{\text{dec}} \exp \left( -\frac{E_{\text{dec}}}{RT} \right) \]  

(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 functions. The rate constant does not accurately represent the turnover frequency of the hydrocarbons on the \(\text{Al}_2\text{O}_3\) surface. The 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 \(\text{CH}_4\) 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 \(k_{\text{dec}}\) 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.

\[ \frac{dC_i}{dt} = R_{\text{dec}} = C_i k_{\text{dec}} \exp \left( -\frac{E_{\text{dec}}}{RT} \right) \]  

(9)

\[ E_{\text{dec}} = p_2 C_i + p_1 C_i + p_0 [\text{mol}^{-1}] \]  

(10)
Combination of Eq. 9 and 10 yields:

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

Which has the analytical solution:

\[
k_{dec} C_M t = \frac{\sqrt{\pi} R T}{\sqrt{2 \sqrt{\pi} p_2 R T}} \text{erfi} \left[ \frac{\sqrt{2} p_1}{2 \sqrt{p_2 R T}} \right] - \text{erfi} \left[ \frac{p_1}{2 \sqrt{p_2 R T}} \right]
\] (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 \( C_c = 15 \) m\(^2\)p,ex, 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.
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 ±15 g.m⁻².pex 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 CH₄ 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 CH₄ conversion over time provides confidence that the kinetics obtained in the single particle reactor can be used to predict CH₄ 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.

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Appendix A. Supplementary data

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

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