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Hydrocarbon pyrolysis with a methane focus: a review on the catalytic effect and the coke production

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ABSTRACT

Hydrocarbon pyrolysis has been widely studied since the 1900's for applications in aerospace as a fuel and/or coolant or for use with fuel cells and hydrogen production with a catalyst. In this context, the role of heterogeneous reactions with homogeneous phase chemistry is unclear despite the fact that it is obviously at the heart of coupled physico-chemical phenomena. In addition, the thermal formation of solid carbon particles -coke, which can be deposited on the structure, impacts the heterogeneous reactions. The aim of this work is to review the available literature on hydrocarbon pyrolysis involving reactions with solid surfaces and coke particles. The influent parameters such as the nature of the fluid, the temperature (up to 2000 K), the pressure (up to 100 bars), the residence time (μ s order to min order), the reactor type (plug flow, batch, perfectly stirred reactor) and the type of catalyst (inert, metallic or more complex such as zeolites) are discussed. Then, a link between catalicity and coke production is addressed. This literature survey focuses in particular on methane because of the growing interest regarding the potential for hypersonic applications.

21 **Keywords:** hydrocarbon pyrolysis, review, catalicity; coke production.

22

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41

42 **1. Introduction**

43 Within the scope of hydrocarbon pyrolysis, various parameters and conditions have been studied,
44 among which: the nature of the reactive fluid (methane [1], propane [2] and other even more complex
45 fluids, such as JP-7 [3]), temperature (from 400 K [4] to more than 2500 K [5]), pressure (from below
46 ambient pressure [6] up to 20 MPa and even more [7]), type of reactor (shock tube [8], flow reactor [9],

47 solar tube [10]), diluted [11] or pure [12] conditions. These experiments and the subsequent results
48 have enabled simple to complex kinetic mechanisms to be constructed in order to describe the chemistry
49 in detail and to perform numerical simulations in a multi-physics configuration. The numerous related
50 works have progressively constituted an accumulation of results which are now diluted in the open
51 literature. Only a few reviews are available and those for methane can be cited [13–15].

52 The surface catalytic effect, which is inherent to the reactor, is an additional complex phenomenon
53 to be considered during hydrocarbon pyrolysis. A number of parameters (the nature of the catalyst, of
54 the pyrolyzed fluid, several products, the ambient conditions, the ratio surface/volume $-S/V$, etc.) play a
55 role and have been initially explored experimentally. From a numerical point of view, proposing kinetic
56 schemes to describe heterogeneous reactions causes a rapid increase in the complexity of the models.
57 Because heterogeneous reactions may be of importance, this justifies details and complex mechanisms
58 being taken into account. Nevertheless, studies on the kinetics of reactions inherent in a large surface
59 (i.e. the inner wall of the reactor) are quite rare. Rather than coating the inner surface of the reactor to
60 study such catalytic effects, an alternative is to place a solid material, a catalyst, inside an inert reactor.
61 Although the chemistry may be quite different, notably regarding the S/V , as suggested by Gordon [16],
62 such data represent a precious source of information regarding heterogeneous chemistry.

63 In parallel, another critical phenomenon is the generation of solid particles. Pyrolysis leads to the
64 production of heavy aromatic compounds which can agglomerate to form a particular type of solid
65 carbon which can both dissolve in the fluid and condense on the reactor wall. Such particles can be
66 classified according to several criteria. As an example, some studies distinguish coke according to its
67 origin: pyrolytic [17], catalytic [18] or also asphaltic [19]. The production of such solid carbon depends
68 on numerous parameters (temperature, pressure, residence, time, surface effect, oxygen content) and its
69 formation has been widely studied in the literature, e.g. [20–22]. The particularity of solid carbon is that
70 it can be deposited on the surface as a thin layer, and, in so doing, can, among other things, deactivate
71 the catalytic sites. Consequently, several studies have been conducted in order to avoid such deposits
72 thereby durably sustaining the activity of the catalysts (e.g. [23–25]).

73 These two phenomena (catalicity and coke production) have generated a large number of data
74 disseminated over the years in the literature. The present paper aims at reviewing the articles related to
75 the catalytic effect and coke production during the thermal decomposition of hydrocarbons (mostly
76 small ones and notably methane). These two issues are linked in several ways: firstly, the catalytic
77 activity can, among other things, modify the production of coke particles (in both ways: enhancement
78 and limitation). Secondly, coke can also have an impact on the catalicity of a material. Indeed, it can
79 stick to the surface of a material and in so doing decrease or even inhibit its effect. The context of this
80 survey is that of regenerative cooling during hypersonic flights, i.e. the endothermic degradation of the
81 fuel which acts as a heat sink. Catalicity and coke production can be critical with respect to the cooling
82 method. Indeed, heterogeneous reactions could occur between the solid material and the fuel. The
83 interactions with the solid materials may either increase or decrease the fuel degradation and this has
84 both direct and indirect consequences on the internal convective cooling of the permeable solid material
85 by the fuel. The direct relationship is due to the pyrolysis rate. When the rate increases, the endothermic
86 effect is higher and the cooling efficiency is thus greater. The indirect relationship is that of the intrinsic
87 formation of coke (coke particles stick inside the pores of the solid material) which is higher for higher
88 pyrolysis rates. This coke layer decreases the heat transfer between the solid and the fluid. As a
89 consequence, cooling efficiency is lower in the case of coke formation. One can also notice that the
90 permeation process (fluid flow) is modified by the coke particles in case of clogging [26,27].

91 A wide review has been proposed of former works specifically concerning methane pyrolysis
92 [15]. This is expected to cover the field of catalicity and coking phenomenon to provide a complete
93 situation of hydrocarbon pyrolysis, particularly as applied to methane which is, as suggested by Davis *et*
94 *al*, a possible efficient fuel (advantageous standard enthalpy of combustion, low price, relatively low
95 coking rate) [28]. This study is mainly devoted to methane. However, it has been widened to include
96 several other hydrocarbons in order to provide complementary information when necessary.

97 **2. Catalytic effect involved in hydrocarbon pyrolysis**

98 Even in the earliest methane pyrolysis investigations, it was observed that several parameters can
99 modify both the kinetic and product ratio. Hurd and Pilgrim [29] pointed out that the species produced
100 during the first instants of decomposition, the contact time, its relationship with the temperature and
101 then, the surface reactor are all parameters to be taken into consideration. Slater [30] worked on the last
102 point and clearly showed that each material has a specific effect on the decomposition rate. Therefore, in
103 most cases, the surface effect was neither considered nor investigated but merely neglected. The catalyst
104 effect may be considered in different ways, namely: the reactor material (metallic, composite), the
105 treatment of the inner wall (e.g. coating) or by a small solid sample insertion. The following subsections
106 investigate these techniques both in order to differentiate the results and to determine the consequences.

107 **2.1 Catalytic effect considering a massive reactor**

108 **2.1.1 Massive reactor: the intrinsic effect of the materials**

109 Studies on the catalytic effect of the inner wall of a reactor are relatively uncommon and were
110 essentially conducted in the 1970's. Before this, few researchers worked on this phenomenon. Thus,
111 Hurd and Pilgrim [29] concluded that the nature of the reactor alters hydrocarbon pyrolysis. They
112 investigated the thermal degradation of butane in a reactor made of iron, nickel or monel (Ni-Cu-Fe
113 alloy) and they noted significant differences with high catalicity for a monel reactor. In comparison,
114 Hurd and Eilers also explored olefin pyrolysis in different metallic reactors and confirmed the high
115 activity of the monel reactor [31]. Regarding iron or nickel, less catalicity was found (decomposition at
116 a lower temperature for the first and modification of the product distribution for the second).

117 Several researchers explored other materials considering different small hydrocarbons. In [32], in
118 propane, ethylene and propylene pyrolysis Crynes and Albright observed little activity for nickel and
119 stainless steel reactors while a non-negligible catalicity for low carbon steel reactors was demonstrated.
120 They also performed tests inside mixed reactors (respectively 30 % and 70 % length of low-carbon steel

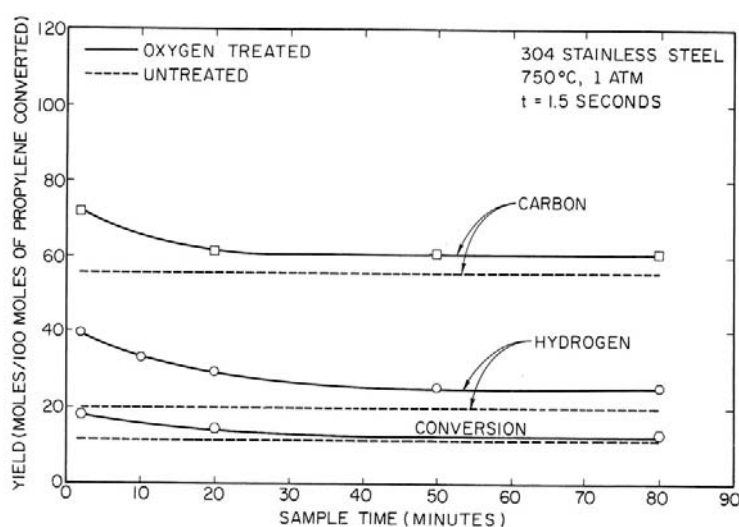
121 and stainless steel) and noticed that a higher activity of low-carbon steel could be observed only if this
122 material was spatially placed after the stainless steel part. Given such results, the authors suggested the
123 role of the surface in the initiation and termination for free radical chain reactions. They also suggested
124 that tubes of small size (i.e. with a high S/V ratio) present enhanced catalytic activity and inherent
125 surface reactions compared with bigger tubes but this is counter-balanced by the nature of the fuel
126 which is considered during the experiment (ethane or propane). Ghaly and Crynes further explored
127 propylene pyrolysis considering more materials [33]. More details are given and notably the nature of
128 the catalicity of each material. There are certain contradictions compared with the previous results.
129 Thus, for the stainless steel reactor, the wall activity is expressed via a higher production of carbon. The
130 low-carbon steel and nickel reactors had a fairly similar profile and demonstrated an increase of activity
131 during the first stage of pyrolysis (coke and hydrogen yield increased) and then it fell and reached a
132 steady-state after one hour. Such a trend suggested a progressive deactivation of the surface by the of
133 solid carbon. Inconel and incoloy reactors showed less activity. Ghaly and Crynes concluded that the
134 wall activity was essentially due to the presence of iron which acts as a catalyst for carbon and hydrogen
135 production. However, the presence of chromium in some alloys inhibits its activity. Therefore, a surface
136 containing an active carbon layer which carries iron atoms (e.g. low-carbon steel) may show higher
137 activity. Concerning nickel, it is assumed that the active sites have a lower affinity with hydrocarbons
138 than iron. Finally, alloys containing both iron and nickel may consequently be less effective than pure
139 metal. Dunkleman and Albright worked on paraffin (ethane and propane) pyrolysis and compared
140 metallic and Vycor glass reactors [2,34]. Significant differences were found between metallic and Vycor
141 reactors but it clearly appeared that the surface reactions had less importance for propane pyrolysis in
142 comparison with ethane experiments. Globally, they noticed that the hydrogen amount and coke
143 formation were lower for Vycor reactors than for metallic ones. In the 2000's, the works of the PRISME
144 laboratory on the catalytic activity of massive reactors constituted recent and quite unique data [35–37].
145 For example, in [37], dodecane pyrolysis was investigated in two different tubular reactors (stainless
146 steel and titanium). Greater pyrolysis activity was noted for the titanium reactor at the same temperature

147 than for a stainless steel one. Indeed the yields of the major products (ethane, ethylene and propane)
148 were multiplied by a factor of 2 while the conversion rate increased from 40 % to 60 %. Nevertheless, it
149 was strange to note that a higher coke deposit was found for the stainless steel tube.

150 These first results demonstrated the mix effect of the catalicity of a reactor. For the same material
151 with the same fluid, substantial differences could be found. Additionally, the catalicity does not only
152 consist in reducing the temperature of hydrocarbon pyrolysis but can also clearly influence certain
153 reaction pathways. Parameters such as time, type of reactor or S/V ratio are of the utmost importance
154 with regard to the catalytic phenomenon.

155 2.1.2 Treatment of the inner surface

156 The treatment of the reactor surface also constituted part of the research investigations on
157 catalicity. In [32], in several cases the reactor was pre-treated (oxygen, hydrogen sulfide, steam, sulfur,
158 anhydrous hydrogen bromide and nitric oxide). Oxygen treatment appeared to drastically affect the
159 product distribution and to be an efficient catalyst for ethylene, propylene and carbonaceous solids
160 (Figure 1).



161
162 **Figure 1. Effect of oxygen pre-treatment. From Crynes and Albright [32]**

163 With regard to hydrogen treatment, it limited the activity while steam had a moderate influence
164 (the conversion increased from 32 % to 35 %). Treatment with hydrogen sulfide inhibited the catalytic

165 effect and was similar to a passivation (subsequent oxygen treatment is ineffective). Other treatments
166 did not significantly affect the hydrocarbon conversion. Ghaly and Crynes explored propylene
167 degradation and confirmed the higher activity for an oxygen pretreated stainless steel reactor but they
168 also noticed that such pretreatment moderated the activity of a low-carbon steel wall (oxygen acts a
169 protective oxide film) [33]. For nickel, this treatment presented no effect for the first 10 minutes before
170 undergoing a great increase due to the partial reduction of the oxide surface layer (by the action of the
171 carbon and hydrogen formed) which led to the formation of a more active nickel. For inconel and
172 incoloy, the results were close to those of oxygen-treated stainless steel. Finally, they found quite
173 different results regarding hydrogen sulfide pretreatment. Thus, a mixed effect was noted for stainless
174 steel (inhibition and then promotion) while a similar effect compared with oxygen was observed for
175 low-carbon steel (passivation). Dunkleman et al. confirmed the passivation effect of hydrogen treatment
176 on the degradation of small paraffin [2,34]. They explained such an effect by the reduction of the
177 surface reactions.

178 The pretreatment of a reactor has a clear impact on catalicity but such effects can clearly differ
179 depending on the materials treated and the treatment itself.

180 **2.1.3 Coated reactor, the example of zeolites**

181 Catalicity should be also studied by considering coated reactors. In this domain, several
182 investigations have been conducted on particular materials such as zeolites or certain of its derivatives
183 [38–41] but generally on heavy hydrocarbons. Zeolites have the great advantage of allowing fuel
184 thermal degradation at lower temperatures whilst reducing the production of coke. The works of Li. *et*
185 *al.* consisted in coating the inner wall of a stainless steel tube by a mixture of different zeolites (HZM-5)
186 and a ceramic-like binder [38]. The pyrolysis of two jet fuels including dodecane was performed under
187 supercritical conditions and within a continuous flow. They demonstrated that the heat sink capacity and
188 conversion were enhanced by the zeolite coating with an increase of about 25 % for the heat sink
189 capacity while dodecane conversion rose from 66 % to 80 %. Zhao *et al.* [39] conducted a similar study

190 with Palladium inside the HZM-5 coating. Pd/HZSM -5 coating presented a better performance than
191 HZSM-5 with a higher rate of conversion (increase of about 10 %) and a promotion of hydrogen yield
192 (about twice as much). The heat sink was also enhanced, even more with the rise of the temperature.
193 Meng *et al.* contributed to the zeolite coating studies by performing supercritical pyrolysis of n-
194 dodecane inside an HZSM-5 coated stainless steel reactor [40]. The authors observed that the
195 conversion of dodecane was higher when the reactor was coated but only up to a certain temperature.
196 Thus, for temperatures of over 848 K, conversion becomes equivalent and even lower than for a nude
197 reactor. This fact is explained by the progressive deactivation of catalytic sites by the filamentous coke.
198 Liu and coworkers further investigated HZMS-5 zeolites under supercritical conditions [42]. They
199 directed their study on the characterization of zeolites and highlighted the relative importance of the
200 particle size. They found that coating a tube with nanoscale zeolites presented certain advantages and
201 notably that of the enhancement of the catalytic activity (more than 1 time). Nevertheless, adhesion on
202 the wall is poorer, but mixing nano- and microscale particles permits this problem to be overcome.

203 The catalicity of zeolite coated reactors is clearly demonstrated and shows interesting abilities
204 namely regarding the reduction of the production of coke. Nevertheless, it must be mentioned that such
205 catalysts are employed only at mid-range temperatures. Consequently, their application in the hottest
206 parts of the cooling channel for jet fuel applications is not currently feasible since zeolites are not active
207 in these conditions.

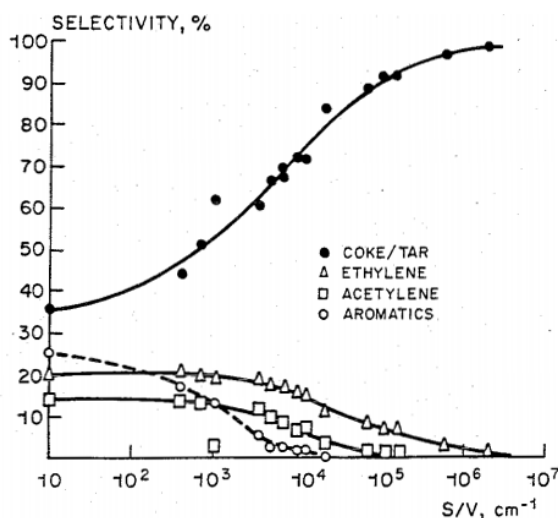
208 **2.2 Effect of small solid catalysts in a pyrolysis reactor**

209 Differentiation of the massive reactor experiments with the catalyst sample is namely motivated
210 by the high importance of S/V ratio or also the contact time with the catalyst. Hence, Gordon [16] was
211 one of the first to experiment its impact on methane pyrolysis. He used a porcelain reactor whose
212 catalytic activity is assumed to be very limited. However, it was demonstrated that this parameter
213 clearly enhances methane decomposition. The pyrolysis rate was even multiplied by a factor of two to
214 three (for an S/V ratio multiplied by 3.5). Later, other research confirmed that this ratio was more or less

215 critical for conversion and product distribution but that its importance was directly linked to the reactor
216 material [2,32–34].

217 2.2.1 Unsupported metallic materials

218 Chronologically, metallic catalysts were investigated first. These catalysts were inserted in reactor
219 considered to be inert (e.g. quartz). The term “unsupported” refers to this inactivity. Fang and Yeh [43]
220 considered 24 metal oxide catalysts deposited on a silica gel. Methane pyrolysis was performed at
221 1400 K and at $2 \cdot 10^{-3}$ MPa in a quartz reactor. The effectiveness of the metals was quantified with regard
222 to C_2 selectivity and decomposition activity. They found that catalysts generally increase methane
223 decomposition but some of them can also decrease it with respect to quartz (e.g. Bi_2O_3/SiO_2). Based on
224 their observations, they suggested a primary mechanism including the catalyst interaction. Van Der
225 Zwet *et al.* conducted a similar study in the presence of different aluminum oxides [44]. The effect of
226 the S/V was confirmed and demonstrated a clear impact on product distribution. The increase in the S/V
227 leads to a progressive decrease in all the species excluding coke and tar (Figure 2).



228

229 **Figure 2. Selectivity to C_2H_4 , C_2H_2 , light aromatics and coke/tar as a function of surface to volume ratio at 25 %**
230 **conversion and 1398 K (reactor volume = 10^{-6} m³) [44].**

231 However, the conversion of methane was poorly affected by increasing the catalytic surface. To
232 explain such a fact, the authors assumed that the radical or dislocation sites of the surface may promote

233 hydrogen abstraction. Moreover, due to the phenomenon of autocatalysis, it may have also an influence
234 on termination (by capturing from the gas phase the species involved in the autocatalysis). Finally, they
235 suggested that a large catalytic surface (aluminum oxide) is favorable to the production of coke and
236 hydrogen while gaseous and liquid products are preferentially produced in a reactor with a low S/V
237 ratio. Wolf *et al.* [45] explored the effect of a platinum catalyst and modeled it over the temperature
238 range of 300 K-700 K. Starting with the experimental results of Belgued *et al.* [46], they created a
239 mechanism composed of 39 elementary surface reactions involving 14 surface species. The kinetic
240 model accounts for the thin monolayer of carbonaceous overlayer which quickly covers the surface of
241 the catalyst. It includes successive steps from the reactant adsorption to the product desorption. Wolf *et*
242 *al.* pointed out that the dominance of a reaction on others depends on the contact time. They presented
243 Ethylidyne (CCH₃) as the determinant species of the mechanism, due to its surface decomposition to C
244 and CH₃ and its influence on ethane production.

245 Zeolites have been also explored as small solid catalysts [e.g. 46–48]. Thus, Xian *et al.* worked on
246 the decomposition of dodecane over HZSM-5 under subcritical and supercritical conditions [48]. They
247 notably found that the activity of the catalyst decreases with the pressure increase and consequently
248 leads to a lower conversion. Such a trend opposes the other results found in the literature (e.g. Dardas
249 and coworkers [49]) and demonstrates, once again, the importance of the reactant and the
250 nature/properties of the catalyst.

251 **2.2.2 Unsupported carbonaceous materials**

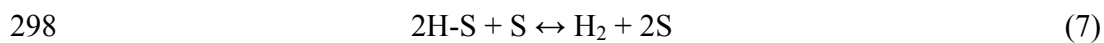
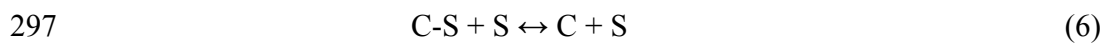
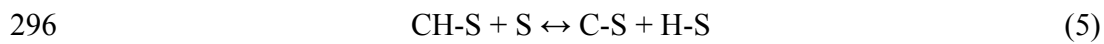
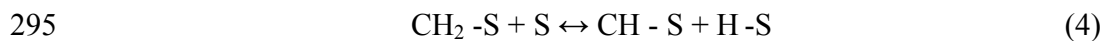
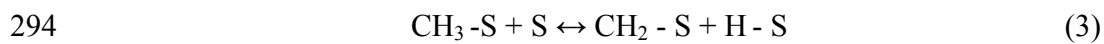
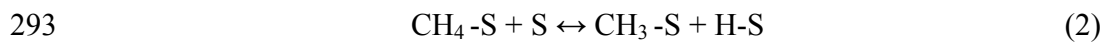
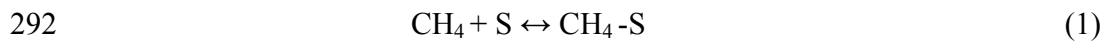
252 With regard to non-metallic catalysts, several studies have been performed using a carbon based
253 catalyst. Hence, Muradov used different types of carbon [50,51]. He determined that graphite and
254 carbon black showed the least activity whereas the initial methane decomposition rate was the highest in
255 the presence of glassy carbon. Lee and coworkers investigated other carbon catalysts (coconut shell and
256 coal) at 850 K [52]. Regarding the nature of the catalyst, they did not observe significant difference in
257 their activity. However, they noted that such a catalyst has good activity at the beginning of the process

258 but is rapidly deactivated by the deposition of coke which blocks the pores. Pinilla *et al.*[53] tested two
259 activated carbons (carbon black) and found a similar trend i.e. high activity but limited as the process
260 progresses but they also noticed that the carbon produced by the degradation of methane can also show
261 a catalytic activity which slightly compensates for the deactivation. Bai *et al.* also explored the activity
262 of commercial activated carbon and compared it with alumina [54]. They observed less (due to the
263 higher activation energy) and different (autocatalytic reaction of carbon production) catalytic activity for
264 the metallic catalyst. They concluded that the methane conversion could be simplified by a two step
265 scheme with the formation of carbon nuclei followed by growth in carbon crystallites. Moliner and
266 coworkers further investigated activated carbon and brought supplementary information about the main
267 characteristics which influence its activity [55]. They concluded that three elements have to be
268 considered: the surface chemistry, the size and the distribution of the pores, and the presence of
269 oxygenated compounds.

270 **2.2.3 Supported materials**

271 It has been demonstrated that not only does the catalyst have an impact on chemistry but the
272 support (i.e. the reactor) can also have a catalytic activity which leads to heterogeneous catalicity. The
273 term “supported” refers to this phenomenon. Ferreira-Aparicio *et al.* specifically studied the interactions
274 between CH₄ and the surface of several catalysts [56]. They exposed the effect of different metallic
275 catalysts (cobalt, nickel, ruthenium, rhodium, iridium and platinum) supported on alumina or silica,
276 thereby demonstrating the importance of the support. Indeed, more hydrogen is produced by the
277 catalysts supported on alumina than those on silica. Ruthenium and iridium were the least efficient
278 catalysts for retaining carbon on their surface while the presence of rhodium on alumina support
279 enhances the production of a more reactive coke (amorphous). Takenaka *et al.* further investigated the
280 support effect on the nickel activity and on its catalytic lifetime [57]. It was observed that SiO₂, TiO₂
281 and graphite supports enhanced methane conversion. Al₂O₃ and MgO had the shortest lifetime. In
282 parallel, they studied the characteristics of coke according to the support and they pointed out certain

283 differences namely regarding the size and the thickness of the carbon filaments. However, Zein *et al.*
 284 [58] found quite different results. They investigated the catalytic decomposition of methane and the
 285 subsequent production of H₂ and of carbon. Nickel was chosen as the catalyst and TiO₂, Al₂O₃, MgO
 286 and SiO₂ were selected as the support. The catalysis was performed at atmospheric pressure and for a
 287 temperature range of 823 K-1173 K. Methane was mixed with argon (1:1 mole) and injected in a
 288 stainless steel reactor where 1 g of the catalyst was placed in its center. They concluded that titanium
 289 oxides were the best support (activity maintained after 2 hours) followed by MgO. The SiO₂ and
 290 moreover, the Al₂O₃ supports had the shortest lifetime. Finally, they proposed a mechanism similar to
 291 the preceding one with regard to carbon and H₂ production:



299 Zadeh and Smith studied the pyrolysis of methane in presence of supported cobalt catalysts (Co-
 300 SiO₂, K-Co-SiO₂, Co-Al₂O₃ and K-Co-Al₂O₃) [59]. A mixture of CH₄ and Ar (respectively 95 % and
 301 5 %) was injected in quartz fixed-bed microreactor heated at 723 K. They observed the so-called Metal
 302 Support Interaction (MSI) which consists in the migration of the SiO₂ support onto the cobalt catalyst.
 303 The MSI increases the methane decomposition activity and the facilitation of the migration of
 304 carbonaceous species from the catalyst surface to the support. This phenomenon was promoted by the
 305 decrease of the initial Co loading. The temperature increase promoted the CH₄ conversion and the metal
 306 coverage. As was mentioned in the previous part, the support also has an effect: conversion is greater
 307 for an alumina support than for a silica support. Finally, the addition of potassium was noticed to
 308 promote the species migration from the metal to the support.

309 Numerous studies have also been conducted on zeolite supported catalysts. Several combinations
310 with different metals have been tested. Xu and Lin have produced a very complete and interesting
311 review on this subject [60]. Globally, it appears that the molybdenum supported on HZSM-5 zeolite
312 presents the best association. Hence, further investigations have been conducted on this combination
313 and by modifying the catalyst preparation. Hence, for example, the works of Solymosi *et al.* who
314 explored methane degradation with unsupported and supported (notably zeolites ZSM-5) molybdenum
315 compounds can be cited [61–63]. According to the nature of the catalyst, its production method, and the
316 nature of the support, substantial differences were observed regarding the pyrolyzed products. The
317 authors also confirmed the progressive deactivation of the catalyst due to the carbon deposition.

318 **2.2.4 Catalicity used for specific purposes**

319 Numerous works on the decomposition of methane with metallic catalysts have been conducted
320 over the past years, but with specific goals. The production of CO₂-free hydrogen is possibly the most
321 important one [64,65]. The works of Shah *et al.* could be cited as an example [66]. They pyrolyzed
322 methane and other different pure and binary metallic catalysts (Fe, Pd, Mo, Ni) supported on alumina at
323 a temperature ranging from 673 K to 1173 K. They pointed out the importance of the pretreatment of
324 such materials: for example, methane is decomposed at a temperature of above 1123 K for a non-treated
325 iron catalyst while the degradation begins 200 degrees lower after oxidization and even lower (723 K) if
326 the catalyst has been previously reduced in a flow of hydrogen and then carburized. They also
327 demonstrated that a binary catalyst (Fe-Mo, Fe-Pd, or Fe-Ni) always possesses higher activity (i.e.
328 production of hydrogen) than a pure one. The production of carbon (e.g. filament) is also a widely
329 studied topic. By way of example, González *et al.* explored the formation of carbon nanotubes using
330 unsupported nanoparticles of nickel as a catalyst [67]. In such studies, the temperature is quite low and
331 the aim is to obtain a fairly low conversion of methane coupled with a moderate carbon growth dynamic
332 in order not to deactivate the catalyst. They tested the adjunction of copper in order to enhance the
333 activity and concluded that such a procedure was inefficient contrary to other experiments with

334 supported nickel catalysts. The third objective is the production of higher (i.e. heavier) hydrocarbons
335 like aromatics.

336 Thus, Holmen proposes an interesting overview of the research conducted in this domain [65]. He
337 points out that the zeolites associated with metals (preferentially molybdenum) are good catalysts and
338 initially enable acetylene and then aromatic compounds (notably benzene) to be formed. All in all, if the
339 interest of such works is undeniable, their purpose is quite far from the present one. For this reason, we
340 do not further review the numerous publications available in the open literature. A very valuable
341 literature survey of Amin *et al.*[68] is helpful to get a better view on the works which are devoted to the
342 three specific objectives mentioned above. The works of Ahmed and coworkers or Abbas and Wan
343 Daud also represent an abundant source of information in this domain [69,70].

344 **3. Investigation on the coke deposits**

345 During the final steps of the pyrolysis of hydrocarbons, solid particles with high carbon content
346 are produced. The so-called “coke” can be deposited on the inner wall of the reactor and it can be found
347 under various natures; Albright *et al.* described seven different types of coke [71]. Thus, the term
348 “coke” reassembles several different particles, which could lead to some confusion. Consequently, in
349 this paper the definition proposed by Fitzer *et al.* [72] shall be employed. Coke is defined as a solid with
350 a high content of the carbon element which is structurally in the non-graphitic state. Hereafter, the terms
351 “coke” and “solid carbon” should be considered as equivalent.

352 Considering the hypersonic application considered in this work, knowledge of coke production is
353 required since its deposit on the surface of the reactor wall has a critical impact on the decomposition of
354 the fuel by changing the thermal equilibrium, modifying the surface catalytic effect and limiting the
355 permeation and the associated cooling of the structure. Particularly, high pressure conditions (and even
356 supercritical states) should be considered when dealing with coke formation. Unfortunately, no work
357 dealing with coke production during supercritical methane pyrolysis was found. It can be noticed that

358 other supercritical fluids have been explored in the open literature and the reader could refer to the
359 following reference for further information [21,73–75].

360 **3.1 Characterization of the coke particles and parameters of influence**

361 Determining the coke characteristics and the parameters which enhance or inhibit its production is
362 important in overcoming the drawback of fuel pyrolysis when used aboard aerospace vehicles.
363 According to the literature, several parameters of importance have a clear influence on coke production.
364 Among them, can be cited: the residence time, the nature of the fluid, the pressure or also the geometry
365 of the reactor [76–83].

366 Blekkan *et al.* [76] studied tar and coke formed during methane pyrolysis in a tubular reactor.
367 First, they highlighted the critical role of acetylene, benzene and PAH formation. They distinguished
368 two types of solid carbon particles: tars containing a high proportion of heavy PAH (e.g. pyrene), come
369 from liquids and stick to the reactor wall, and soot, formed in the gas phase from reactive species like
370 acetylene. They pointed out a first parameter of influence on coke production which is the residence
371 time. It was observed that coke selectivity reaches about 80 % for a residence time of 1 second while it
372 is only 20 % for 0.5 s. Guéret *et al.* confirmed the role of residence time and added more details. But
373 contrary to Blekkan *et al.*, they distinguish three types of coke and also work on the temperature
374 influence [77]. Globally, they classified the solid carbon deposit as follows: graphitic type which is
375 produced whatever the residence time (it seems to act as an initial layer) and is predominant for
376 temperatures of over 1423 K; amorphous (carbon black) whose production increases with the residence
377 time and is maximal between 873 K and 1423 K; and soot which is produced for short residence times
378 (lower than 0.6 s) and at low temperatures (573 K – 873 K). Albright and Marek confirmed the critical
379 importance of the residence time (considering longer periods than the previous one), but also added two
380 other parameters which are the geometrical features of the surface and the time of operation [78]. They
381 pyrolyzed acetylene and toluene in a Vycor glass tubing reactor where two rectangular specimens were
382 placed. The amount of solid carbon and the nature of the coke were different depending on the residence

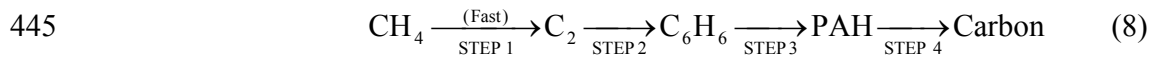
383 time, the length of the pyrolysis run, the position of the specimen and its nature. Regarding the coking
384 rate, two maxima could be reached for different residence times (3 s and then 9 s). They assumed that
385 this signals the existence of two different mechanisms as a function of the production of certain
386 precursors. The morphology of the coke significantly varies with the residence time. Thus, spherical
387 coke particles whose size increases with the residence time and filamentous carbon which is produced
388 preferably for a second order residence time were observed. Geometrical factors, such as the way the
389 specimen is inserted in the reactor or the S/V ratio, play a significant role and this impacts the coke
390 quantity, the particle size and the coking rate. In addition, the morphology changed significantly along
391 with the progress of the coke production (increase of the diameters of both the spherical and filamentous
392 coke). The nature of the specimen (incoloy, stainless steel, quartz, and vycor) also affected the coke
393 production with a higher value for the metallic one. The authors suggested that heterogeneous reactions
394 can enhance or limit the coke deposition and its nature. This will be discussed later. Finally, Albright
395 and Marek [78] also observed that the length of the experiment can also modify the morphology of the
396 carbon particles. This could signal a modification of the coking mechanism during the progress of the
397 production process. Dunkleman and Albright demonstrated and quantified the influence of the surface
398 [34]. They estimated the deposition rate for three reactors and determined the following ascending
399 order: vycor glass, incoloy and then stainless steel. Additionally, it was observed that the S/V ratio has
400 an impact, i.e. the higher S/V, the larger the carbon deposit. A mechanistic model of 18 reactions was
401 developed in complement to their experimental data. Due to the very limited results, the model did not
402 integrate surface reactions but “suppressed” them by correcting the initial reaction rates of the
403 “classical” reaction pathway and simulating a surfaceless experiment. Such a correction permitted good
404 agreement to be obtained between numerical predictions and experimental results. Altin and Elser
405 [79,80,84] also explored the impact of the surface and compared the deposition of carbon, from JP-8
406 pyrolysis, on several surfaces and notably on two superalloys (Inconel 600 and Inconel X). The carbon
407 deposition was 15 times higher for Inconel 600 than for Inconel X. Filamentous carbon coated by a
408 carbonaceous layer remained on Inconel 600 while both crystalline and amorphous carbons were

409 deposited on Inconel X. Such differences are explained by the presence of several elements (e.g. Ti or
410 Al) which act as carbon deposit inhibitors. Gascoin *et al.* conducted similar investigations [20] by
411 performing dodecane pyrolysis experiments in stainless steel, low carbon steel and titanium tubular
412 reactors. They provided the characteristics of the coke produced thanks to SEM observations, EDS, X-
413 ray and FTIR analysis. The coke has different aspect as a function of reactor nature (e.g. for stainless
414 steel tube, millimetric aggregates constituted from micrometric particles were mainly formed inside the
415 fluid flow while for steel reactors, the deposit appeared as very dry sticky shavings). They found spatial
416 heterogeneous deposit along the reactor. The increase of the residence time or of the pressure enhances
417 the formation of coke while the production of solid carbon has been linked to methane formation. In
418 [81]. Reyniers *et al.* confirmed the role of pressure in the increase of the carbon productions. Lucas and
419 Marchand pyrolyzed methane in a tubular reactor while modifying the temperature, the pressure and the
420 flow rate [82]. They observed that the temperature and flow rate did not impact the density of the coke
421 particles, the increase of pressure led to a decrease in the density. Naturally, the studies mentioned
422 above are just a fraction of the numerous works which are available in the literature (e.g. studies on the
423 effect of the surface on coke production, Ref.[85–90]). As explained by Oberlin in her excellent review
424 [83], a considerable quantity of research has been performed under a very wide panel of conditions. This
425 is why the results are so mixed and, sometimes, contradictory. This is why the first part of this paper
426 aims at isolating the works which present the main information related to the influent parameters on
427 coke production. Thus, it has to be noted that the increase of the pressure, the temperature and the
428 residence time favor coke production. Regarding a hypersonic application, the first two parameters are
429 not easy to control efficiently. On the contrary, acting on the residence time in order to shorten it but
430 also using specific materials are parameters which appear, to a certain extent, more controllable.

431 **3.2 Modeling the coke formation and its coupled impact on surface deactivation**

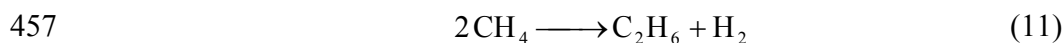
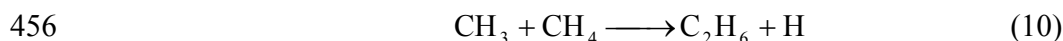
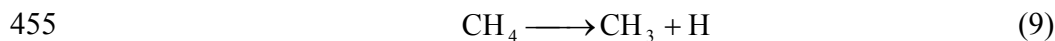
432 Guéret *et al.* [77] studied the solid carbon production from the methane pyrolysis and they
433 proposed an extensive literature survey. Their conclusion was that coke formation begins with the

434 formation of radicals from hydrocarbon degradation. Then, condensation and polymerization reactions
 435 lead to the production of some “complexes” (intermediates molecules in the formation of coke). At this
 436 point, there are two possibilities: on the one hand, adsorption of complexes at the surface and formation
 437 of an anisotropic pyrolytic carbon layer or on the other, condensation and polymerization of these in the
 438 gas phase. This last pathway is faster than the first one and generates a dispersed carbon with an
 439 isotropic structure (the so-called carbon black). Lucas and Marchand supplied a first approach for
 440 modeling the coking mechanism in case of methane pyrolysis [82]. They determined that C₂
 441 hydrocarbons (acetylene and ethylene) and benzene were the most represented light species while
 442 naphthalene, anthracene, phenanthrene, acenaphtylene, pyrene and fluoranthrene were found to be the
 443 most common PAHs. Based on those results, Lucas and Marchand proposed the following simple
 444 mechanism divided into 4 steps:

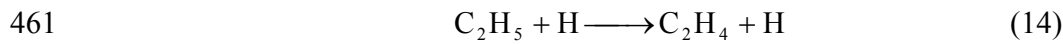
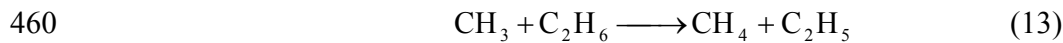
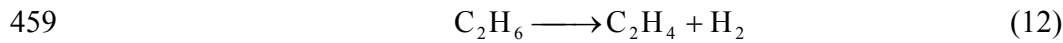


446 They noted that the C₂ species had an essential role in the formation of benzene and of different
 447 PAHs. Considering the kinetics of the reactions, they assumed that methane dissociation coefficient had
 448 practically no influence on the production of C₂ because of the rate of the first step. On the contrary, a
 449 low dissociation coefficient of methane would decrease the formation of benzene and PAH while for a
 450 higher one, the production of benzene and PAH would initially increase before diminishing. The authors
 451 observed that carbon was more actively produced by reactions involving anthracene than the other
 452 PAHs. This simple mechanism was used and extended by Benzinger *et al.* [91]. They divided the coking
 453 phenomenon into five steps beginning with the cracking of methane:

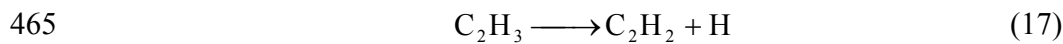
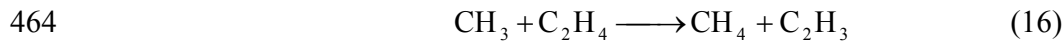
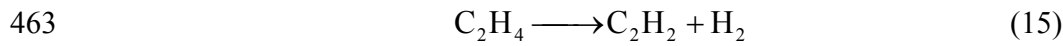
454 STEP 1: From to methane to ethane:



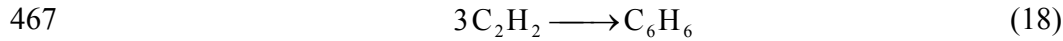
458 STEP 2: From ethane to ethylene:



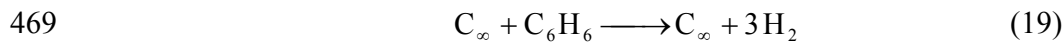
462 STEP 3: From ethylene to acetylene:



466 STEP 4: From acetylene to benzene:



468 STEP 5: Growth of solid carbon (C_∞):

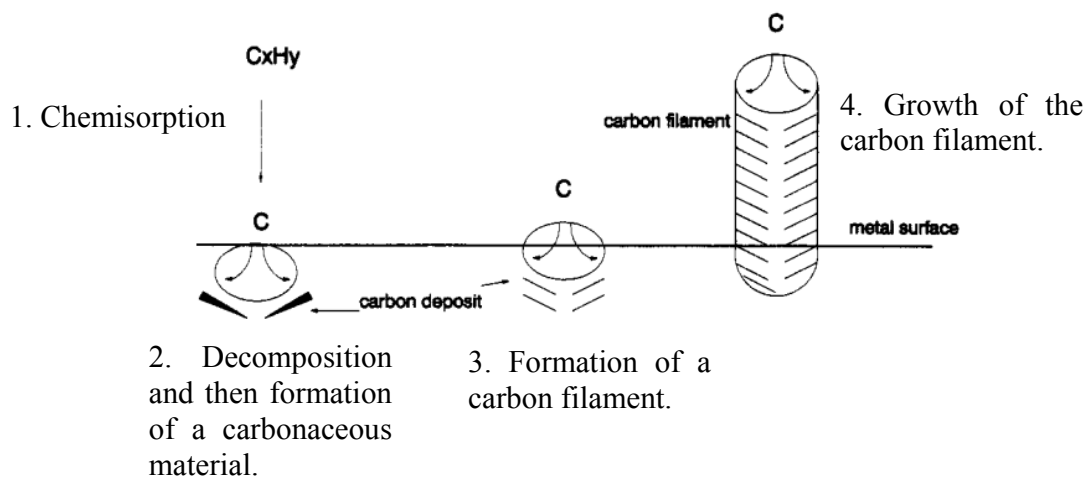


470 So, methane first cracks into C_2 hydrocarbons. The condensation of acetylene leads to benzene
 471 and finally to the growth of carbon particles. Even if other compounds contribute to the coking
 472 phenomenon, benzene remains the most important intermediate species. Becker and Hüttinger followed
 473 their investigations on coking and performed experiments [92]. The authors observed the following
 474 elements. First, they found that the C_1 -species can form coke directly. Secondly, the deposit rate shows
 475 an exponential increase with residence time. Thirdly, the increase of the initial partial pressure leads to
 476 the raise of C_1 to C_6 species with a plateau for ethane, ethylene and acetylene. Finally, hydrogen
 477 decreases coke production by saturating the free radical active sites. This leads to a critical fall of
 478 acetylene and of benzene formation. Based on those elements, the authors proposed a basic coke
 479 formation scheme where coke can be directly formed from numerous hydrocarbons including methane
 480 itself. It was also demonstrated that ethylene is not only formed from ethane, acetylene not only from
 481 ethylene and benzene not only from acetylene. These last assertions clearly reveal that a realistic coking
 482 mechanism involves a high number of reactions. Albright and Marek proposed a relatively more

483 complex model [93]. They combined three distinct -but linked- mechanisms. The first one (the so-called
 484 mechanism 1) considers the catalytic effect of the reactor and involves metal-catalyzed reactions. The
 485 coke produced by such a mechanism is filamentous and often contains metal. Acetylene is a
 486 predominant precursor while metal carbides are considered as intermediate compounds and iron and
 487 nickel as catalysts. Such coke is produced at temperatures ranging from 673 K to 1323 K. Mechanism
 488 number 2 highlights the importance of aromatics species (Ar-H) as intermediate in the formation of
 489 coke. A majority of those compounds come from acetylene. The following schematic sequence
 490 describes the production of solid carbon:



492 This coke is metal-free and does not appear below 973 K. The last mechanism describes the
 493 growth of the coke layer involving microspecies (generally acetylene) with the free radicals (methyl,
 494 ethyl, phenyl or benzyl radicals) on the coke surface forming aromatic rings. Hence, the authors
 495 concluded that acetylene is essential in the production of solid carbon as it produces the majority of
 496 coke precursors. Reyniers *et al.* confirmed this assumption of three combined mechanisms thanks to
 497 experimental data [81]. They conducted coking experiments considering feedstock from methane to
 498 complex fuels like kerosene; in presence of H₂O or N₂. Their main conclusions were: the light species
 499 like methane and ethane produce more coke than heavier molecules; more coke is found during the
 500 pyrolysis of isoparaffin than of normal paraffin; the presence of steam relatively inhibits the coke
 501 deposit by removing it at temperatures of over 1123 K; the solid carbon yield rises with the increase in
 502 pressure. Based on these observations, Reyniers *et al.* assumed that the carbon layer deposition depends
 503 on the contribution of three mechanisms. The first one is similar to the mechanism 1 described by
 504 Albright and Marek [93]. It consists in a heterogeneous catalytic mechanism which is predominant in
 505 the initial phase with a high rate of carbon deposition. Figure 3 presents a schematic view of this
 506 deposition.



507

508 **Figure 3. Heterogeneous catalytic mechanism of carbon deposition. Taken from Reyniers et al. [81].**

509 This carbon layer is a porous structure where active sites permit coke deposition via a non-
 510 catalytic mechanism. Indeed, the covering of the metal surface leads to a progressive decrease in coke
 511 formation by this catalytic method. The second mechanism, described by the author as the
 512 “Heterogeneous Noncatalytic Mechanism”, is the predominant one. It consists of the decomposition of
 513 hydrocarbons into aromatic structures and then into graphitic coke filaments. The polyaromatic layer is
 514 progressively dehydrogenated by free radicals which are present in the gas phase. The number of
 515 possible reactions is very large and depends on the nature of the feedstock. The last mechanism is
 516 described as homogeneous and noncatalytic. It involves the formation of PAH in the gas phase. These
 517 molecules agglomerate into tar droplets which generally adhere to the surface and are incorporated in
 518 the coke layer. This pathway prevails for heavy liquid feedstock and at temperatures of over 1173 K.
 519 Since acetylene and PAH are the keys for the production of solid carbon, it could be of interest to take a
 520 quick look at this (e.g. [94–97]). The works of Böhm *et al.* [94,95] could be cited as an example for the
 521 present review. They studied the growth of PAH and the formation of soot experimentally during the
 522 pyrolysis of acetylene and of benzene at high temperature and pressure. The PAH formation model that
 523 they developed was based on three reaction pathways. First, the H-abstraction is associated with C_2H_2
 524 addition to aromatics (e.g. acetylene addition to naphthalene forming phenanthrene and pyrene): the so-
 525 called HACA route. Then, combination reactions involve phenyl with benzene, the so-called ring-ring

526 condensation. Finally, cyclopentadienyl is recombined (i.e. naphthalene may be formed without
527 benzene). As a conclusion, PAH growth is more dependent on the ring-ring condensation than on the
528 HACA route for short residence times. Benzene is consequently the most efficient precursor in
529 comparison with acetylene. On the contrary, for longer residence times, the benzene consumption infers
530 the dominance of acetylene as PAH precursor. The HACA route becomes essential. Equally, the optimal
531 soot production is reached when these two mechanisms work “hand in hand”. Finally, the
532 cyclopentadienyl pathway is important during acetylene pyrolysis.

533 **3.3 Catalicity and coke**

534 As is mentioned in the previous parts, the presence of a catalyst (reactor surface or solid) can
535 modify the course of coke formation (enhancement or limitation) [2,33,34,44,56,78–80,84–90]. In
536 addition, in the presence of a catalyst, another type of coke can be produced i.e. catalytic coke. If this is
537 generally observed as different forms, catalytic coke is mostly formed as a filamentous carbon [98,99].
538 Schematically and considering a metallic surface, the production of filamentous carbon can be
539 summarized as follows: first, the hydrocarbon is adsorbed on the surface; reactions occur and some coke
540 particles are formed; then, carbon atoms are progressively dissolved and diffuse through the metal
541 particles; an accumulation occurs which leads to a certain tension; the metal particles are removed from
542 the surface and will act as active sites in the production of catalytic coke; a carbon filament is
543 progressively formed with metal particles at its topside. Equally, the coke could affect catalicity
544 generally by covering the reactive sites (i.e. catalytic deactivation). First, it must be mentioned that
545 several reviews have been proposed on catalytic deactivation namely due to coke deposition,
546 particularly during the last 70s and 80s. Precious information can be found and reference may be made
547 to the following works for complements: Rostrup-Nielsen and Trimm [100]; Butt and Billimoria [101];
548 Trimm [102] or more recently Bartholomew [103]. Secondly, to the authors’ knowledge, no works are
549 available regarding catalytic methane pyrolysis with coke production and catalyst deactivation.
550 Consequently, this review has been extended to other hydrocarbons through the presentation of the

551 works of Guisnet and Magnoux [104–106]. In Ref.[104,105], they compared the thermal degradation of
552 n-heptane with 4 different zeolites (USHY, HMOR, HZSM5 and HERI). They evaluated the coking
553 impact on deactivation, which varies according to the nature of the zeolite. HMOR, HERI and, to a
554 lesser extent, USHY deactivates quickly contrary to HZSM5 whose deactivation is slow. The
555 deactivation is about 40 times greater for HERI, 15 times for HMOR, 3 times for USHY than for
556 HZSM5. The structure and the size of the zeolite pores on the one hand and the density of acid sites on
557 the other are responsible for this difference between zeolites. The modes of deactivation are the
558 limitation of the access (for low coking rates, particularly predominant with HSZM5) or the total
559 blockage of the access (predominant for HMOR and HERI) of the catalytic sites. In Ref.[106], Guisnet
560 and Magnoux presented some propositions in order to limit this unwanted deactivation. They isolated 3
561 points: adapting the pore structure by preferentially chose zeolites without trapping cavities; adjusting
562 the acidity of catalytic sites in order to obtain good homogeneity and finally, setting efficient operating
563 conditions in order to avoid the blockage of pores. Paweewan *et al.*[107] also worked on “zeolite
564 deactivation” during n-hexane degradation. They provided the main characteristics of coke particles and
565 they explained its effect on deactivation which was quite different compared with the previous case.
566 Indeed, its effect was attributed to “selective site poisoning” (i.e. the removing of the predominant
567 active sites) instead of pore blockage.

568 Froment and coworkers[108–116] studied the deactivation of numerous catalysts (zeolites, metal)
569 with regard to coke deposition. They developed models in order to predict this phenomenon by
570 assessing the concept of site coverage and pore blockage. The particularity of this model is that time is
571 not taken into account. For example, the deactivation function φ_A (regarding the site coverage) for a
572 given reaction (e.g. $A \rightarrow B$) is defined as:

$$573 \quad \varphi_A = \left(\frac{C_t - C_{Cl}}{C_t} \right)^{n_A} \quad (21)$$

574 with $n_A = 1$ (single site main reaction) or 2 (dual site main reaction), C_t = total concentration of
575 active sites and C_{Cl} = concentration of sites covered with coke or coke precursor.

576 As a consequence, the rate r_A of this reaction is modified as follows:

$$577 \quad r_A = r_A^0 \varphi_A \quad (22)$$

578 with $0 \leq \varphi_A \leq 1$ and r_A^0 is the initial rate in absence of coke.

579 It must be noted that the deactivation of the catalyst directly affect the coke formation so that Eq.
580 22 is also valid for the coke rate Since these equations are not sufficient for global deactivation to be
581 taken into account, namely regarding the probability of pore blockage, Froment *et al.* explained that it is
582 necessary to develop a model using probability theory and considering the geometry of the catalysts as a
583 network of pores. For example, in Ref.[110] they suggested a complex model of four different catalyst
584 networks. In Ref.[112], they improved this model by taking into account the diffusion limitation. In the
585 early 2000s, Froment published a complete work on catalyst deactivation [116]. He divided his
586 approach according to three levels: the active sites, the catalyst particle and the reactor (referring to the
587 previous equations used for particle level and adding equations which describe the temperature and the
588 concentration evolutions).

589 Among other works from the 90s and 2000s (e.g. Ref. [48,117–122]), Beltramini *et al.*[117]
590 studied coke production and the deactivation effect on a bifunctional catalyst (metallic and acidic)
591 according to different metal contents. They highlighted the different trends between metallic and acid
592 sites, the first one being more affected by coke production (i.e. quick deactivation) and acting as a
593 regulator on the coke production because of its involvement in the precursors of coke. Forzatti and Lietti
594 proposed a review on catalyst deactivation dealing with its main causes [119]: poisoning, coking or
595 sintering phenomena. They exposed an example of catalyst deactivation considering a fluid catalytic
596 cracking model. Finally, Reyniers *et al.* [120,121] pointed out other important notions regarding the
597 coke. They demonstrated its influence on several chemical reactions during the pyrolysis of several
598 hydrocarbons: n-hexane, 2,2,4 triMe-pentane, propene, and i-butene. They showed the influence of the
599 gas phase composition on the coking rate, notably the positive effect of olefins. The coke molecules can
600 form carbenium ions and they act as hydride donors and, consequently, they interact and they intervene

601 in the formation of catalytic products. For example, regarding the hexane degradation, the formation and
602 the presence of coke favors the selectivities of C₁ and C₂ hydrocarbons. Finally, the reaction rates can be
603 positively or negatively influenced by the coke formation according to the reaction type, the coke
604 content and the acid sites properties.

605 **4. Conclusions**

606 Pyrolysis involves a complex kinetic mechanism in the homogeneous phase whatever the initial
607 fuel composition to be considered and this becomes even more challenging when considering
608 heterogeneous reactions with a surface reactor and the formation of solid coke particles. Through the
609 literature survey presented in this work, a wide variety of experimental conditions has been presented.
610 The understanding of all the coupled phenomena which occur is not simple and numerous parameters
611 have to be considered. The nature of the inner wall drastically affects the course of thermal degradation.
612 Regarding this aspect, several elements are of importance. If the nature of the catalyst seems to be an
613 obvious factor, others should be mentioned and must be considered and in particular: the temperature,
614 the pressure, the nature of the fuel and the S/V ratio. Equally, interesting parallel parameters have been
615 assessed such as the pretreatment of the reactor or the support of the catalyst which can significantly
616 modify the catalytic activity. Several kinetic models have been developed. Studying the interaction
617 between gas species and active sites has become more complex by considering its potential deactivation
618 namely by solid carbons produced during pyrolysis. The so-called coke is an unwanted product which
619 can be of different natures, diluted in the gas phase and deposited at the surface of the reactor wall. In so
620 doing the catalytic activity is drastically reduced which impacts the kinetics of the reaction. Several
621 works have demonstrated the possibility of decreasing such an undesired process namely by pre-treating
622 the surface or setting efficient conditions.

623 Studying such effects is incontrovertible regarding the context of regenerative cooling thanks to
624 the endothermic degradation of fuel during hypersonic flights. If several studies are available, it is
625 undeniable that there remains a clear lack in this domain with regard to methane and namely regarding

626 the interaction between this fluid and its pyrolyzed product with materials of interest (i.e. composites).
627 The operating conditions should be intensively explored within the scope of limiting coke production.

628 **5. Acknowledgments**

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