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

Guillaume Fau, Nicolas Gascoin, Johan Steelant

Hydrocarbon pyrolysis with a methane focus: a

review on the catalytic effect and the coke production

Guillaume Fau,[*a] *Nicolas Gascoin,*[b] *and Johan Steelant*[c]

[a]University of Orleans, INSA-CLV, 88 boulevard Lahitolle – 18000 Bourges, France.

[b]INSA-CLV, 88 boulevard Lahitolle – 18000 Bourges, France.

[c]European Space Research and Technology Centre, Keplerlaan 1, 2201 AZ Noordwijk, The Netherlands

*Corresponding author: Tel.: +33 2 48 23 40 97. E-mail: guillaume.fau@univ-orleans.fr

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 (μs 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 calicity and coke production is addressed. This literature survey focuses in particular on methane because of the growing interest regarding the potential for hypersonic applications.

1. Introduction

Within the scope of hydrocarbon pyrolysis, various parameters and conditions have been studied, among which: the nature of the reactive fluid (methane [1], propane [2] and other even more complex fluids, such as JP-7 [3]), temperature (from 400 K [4] to more than 2500 K [5]), pressure (from below 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, modifythe 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 doingdecrease 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.

2. Catalytic effect involved in hydrocarbon pyrolysis

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

2.1 Catalytic effect considering a massive reactor

2.1.1 Massive reactor: the intrinsic effect of the materials

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

Several researchers explored other materials considering different small hydrocarbons. In [32], in propane, ethylene and propylene pyrolysis Crynes and Albright observed little activity for nickel and stainless steel reactors while a non-negligible catalicity for low carbon steel reactors was demonstrated. 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
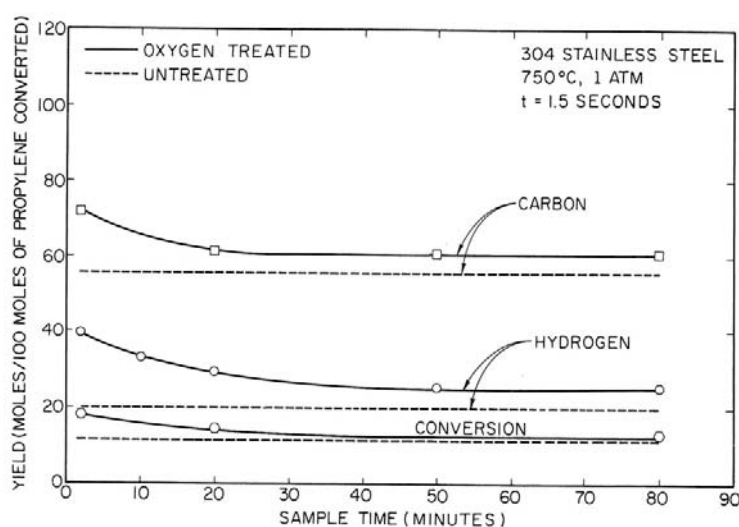
162 **Figure 1. Effect of oxygen pre-treatment. From Crynes and Albright** [32]

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

7

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 over848 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].

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 2.10^{-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

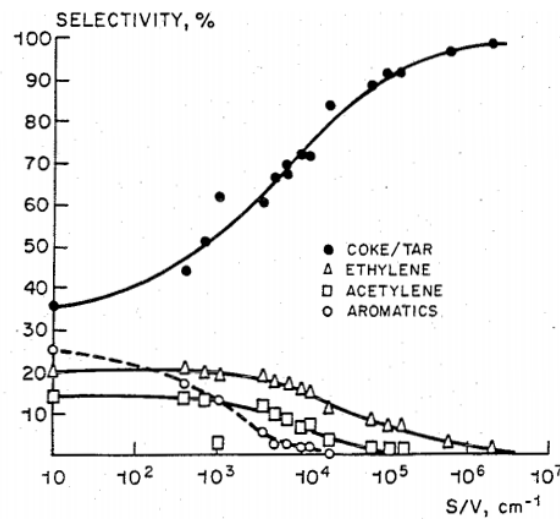229 **Figure 2. Selectivity to C_2H_4, C_2H_2, light aromatics and coke/tar as a function of surface to volume ratio at 25 %**

230 **conversion and 1398 K (reactor volume = 10^{-6} m^3) [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

hydrogen abstraction. Moreover, due to the phenomenon of autocatalysis, it may have also an influence on termination (by capturing from the gas phase the species involved in the autocatalysis). Finally, they suggested that a large catalytic surface (aluminum oxide) is favorable to the production of coke and hydrogen while gaseous and liquid products are preferentially produced in a reactor with a low S/V ratio. Wolf *et al.* [45] explored the effect of a platinum catalyst and modeled it over the temperature range of 300 K-700 K. Starting with the experimental results of Belgued *et al.* [46], they created a mechanism composed of 39 elementary surface reactions involving 14 surface species. The kinetic model accounts for the thin monolayer of carbonaceous overlayer which quickly covers the surface of the catalyst. It includes successive steps from the reactant adsorption to the product desorption. Wolf *et al.* pointed out that the dominance of a reaction on others depends on the contact time. They presented Ethylidyne (CCH_3) as the determinant species of the mechanism, due to its surface decomposition to C and CH_3 and its influence on ethane production.

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

2.2.2   Unsupported carbonaceous materials

With regard to non-metallic catalysts, several studies have been performed using a carbon based catalyst. Hence, Muradov used different types of carbon [50,51]. He determined that graphite and carbon black showed the least activity whereas the initial methane decomposition rate was the highest in the presence of glassy carbon. Lee and coworkers investigated other carbon catalysts (coconut shell and coal) at 850 K [52]. Regarding the nature of the catalyst, they did not observe significant differencse in 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 withthe 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 CH_4 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 SiO_2, TiO_2

281   and graphite supports enhanced methane conversion. Al_2O_3 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 H_2 and of carbon. Nickel was chosen as the catalyst and TiO_2, Al_2O_3, MgO

286 and SiO_2 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 SiO_2 and

290 moreover, the Al_2O_3 supports had the shortest lifetime. Finally, they proposed a mechanism similar to

291 the preceding one with regard to carbon and H_2 production:

292
$$CH_4 + S \leftrightarrow CH_4\text{-}S \tag{1}$$

293
$$CH_4\text{-}S + S \leftrightarrow CH_3\text{-}S + H\text{-}S \tag{2}$$

294
$$CH_3\text{-}S + S \leftrightarrow CH_2\text{-}S + H\text{-}S \tag{3}$$

295
$$CH_2\text{-}S + S \leftrightarrow CH\text{-}S + H\text{-}S \tag{4}$$

296
$$CH\text{-}S + S \leftrightarrow C\text{-}S + H\text{-}S \tag{5}$$

297
$$C\text{-}S + S \leftrightarrow C + S \tag{6}$$

298
$$2H\text{-}S + S \leftrightarrow H_2 + 2S \tag{7}$$
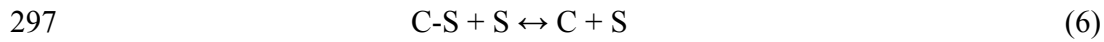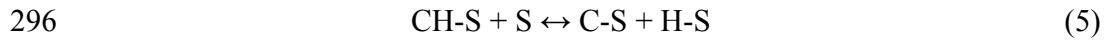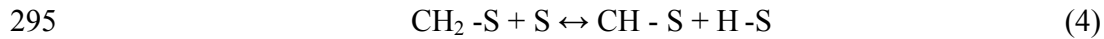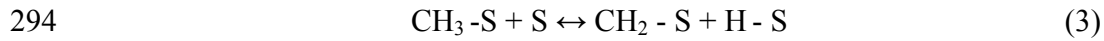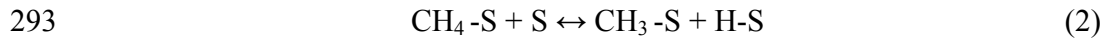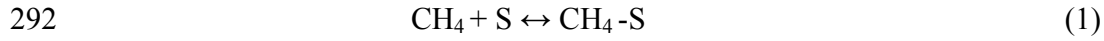
299 Zadeh and Smith studied the pyrolysis of methane in presence of supported cobalt catalysts (Co-

300 SiO_2, K-Co-SiO_2, Co-Al_2O_3 and K-Co-Al_2O_3) [59]. A mixture of CH_4 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 SiO_2 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 CH_4 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 CO_2-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
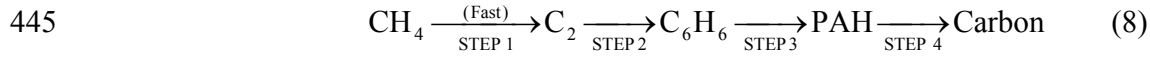
383   time, the length of the pyrolysis run, the position of the specimen and its nature. Regarding the coking

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**
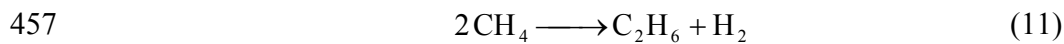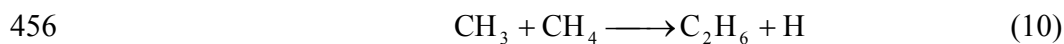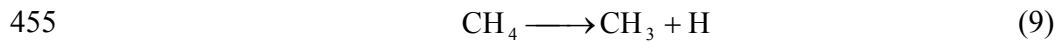
432   Guéret *et al.* [77] studied the solid carbon production from the methane pyrolysis and they

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 C_2

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:

445
$$CH_4 \xrightarrow[\text{STEP 1}]{\text{(Fast)}} C_2 \xrightarrow[\text{STEP 2}]{} C_6H_6 \xrightarrow[\text{STEP 3}]{} PAH \xrightarrow[\text{STEP 4}]{} Carbon \qquad (8)$$

446 They noted that the C_2 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 C_2 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 initally 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:

455
$$CH_4 \longrightarrow CH_3 + H \qquad (9)$$

456
$$CH_3 + CH_4 \longrightarrow C_2H_6 + H \qquad (10)$$

457
$$2CH_4 \longrightarrow C_2H_6 + H_2 \qquad (11)$$

458 STEP 2: From ethane to ethylene:

459
$$C_2H_6 \longrightarrow C_2H_4 + H_2 \qquad (12)$$

460
$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \qquad (13)$$

461
$$C_2H_5 + H \longrightarrow C_2H_4 + H \qquad (14)$$
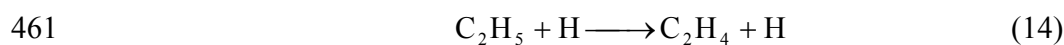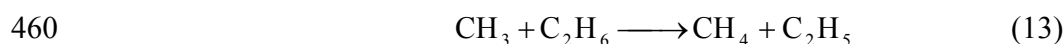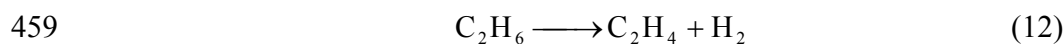
462
STEP 3: From ethylene to acetylene:

463
$$C_2H_4 \longrightarrow C_2H_2 + H_2 \qquad (15)$$

464
$$CH_3 + C_2H_4 \longrightarrow CH_4 + C_2H_3 \qquad (16)$$

465
$$C_2H_3 \longrightarrow C_2H_2 + H \qquad (17)$$

466
STEP 4: From acetylene to benzene:

467
$$3\,C_2H_2 \longrightarrow C_6H_6 \qquad (18)$$
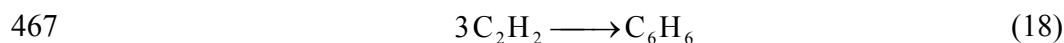
468
STEP 5: Growth of solid carbon (C_∞):

469
$$C_\infty + C_6H_6 \longrightarrow C_\infty + 3\,H_2 \qquad (19)$$
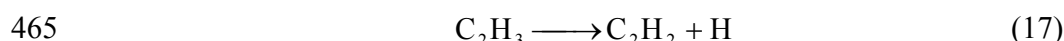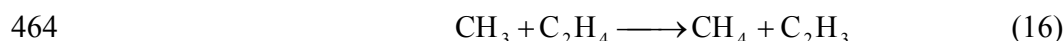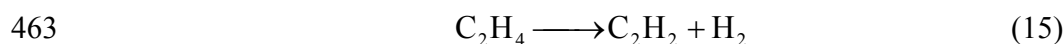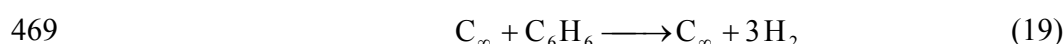
470   So, methane first cracks into C_2 hydrocarbons. The condensation of acetylene leads to benzene

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

20

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:

491
$$nAr-H \xrightarrow{-H_2} tars \xrightarrow[condensation]{nucleation} tar\,droplets \xrightarrow{-H_2} semitar\,droplets \xrightarrow{-H_2} coke \qquad (20)$$
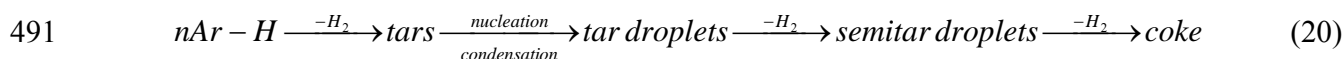
492 This coke is metal-free and does not appear below 973 K. The last mechanism describes the

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 H_2O or N_2. 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.

1. Chemisorption

4. Growth of the carbon filament.

carbon filament

metal surface

C

2. Decomposition and then formation of a carbonaceous material.

3. Formation of a carbon filament.
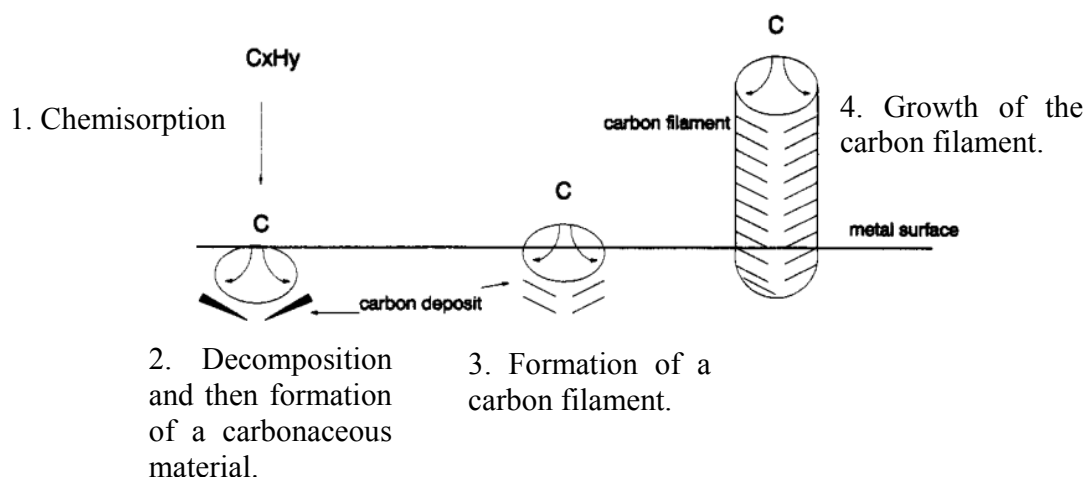
carbon deposit

CxHy

507

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

This carbon layer is a porous structure where active sites permit coke deposition via a non-catalytic mechanism. Indeed, the covering of the metal surface leads to a progressive decrease in coke formation by this catalytic method. The second mechanism, described by the author as the "Heterogeneous Noncatalytic Mechanism", is the predominant one. It consists of the decomposition of hydrocarbons into aromatic structures and then into graphitic coke filaments. The polyaromatic layer is progressively dehydrogenated by free radicals which are present in the gas phase. The number of possible reactions is very large and depends on the nature of the feedstock. The last mechanism is described as homogeneous and noncatalytic. It involves the formation of PAH in the gas phase. These molecules agglomerate into tar droplets which generally adhere to the surface and are incorporated in the coke layer. This pathway prevails for heavy liquid feedstock and at temperatures of over 1173 K. Since acetylene and PAH are the keys for the production of solid carbon, it could be of interest to take a quick look at this (e.g. [94–97]). The works of Böhm *et al.* [94,95] could be cited as an example for the present review. They studied the growth of PAH and the formation of soot experimentally during the pyrolysis of acetylene and of benzene at high temperature and pressure. The PAH formation model that they developed was based on three reaction pathways. First, the H-abstraction is associated with C_2H_2 addition to aromatics (e.g. acetylene addition to naphthalene forming phenanthrene and pyrene): the so-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
$$\varphi_A = \left(\frac{C_t - C_{Cl}}{C_t} \right)^{n_A} \qquad (21)$$

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
$$r_A = r_A^{0} \varphi_A \qquad (22)$$

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 C_1 and C_2 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**

630 **6. References**

631 [1] Q. Sun, Y. Tang, G. Gavalas, Methane pyrolysis in a hot filament reactor, Energy Fuels. 14
632   (2000) 490–494.

633 [2] J. Dunkleman, L. Albright, Pyrolysis of propane in tubular flow reactors constructed of different
634   materials, in: Ind. Lab. Pyrolyses, American Chemical Society, 1976: pp. 261–273.

635 [3] H. Huang, D. Sobel, L. Spadaccini, Endothermic heat-sink of hydrocarbon fuels for scramjet
636   cooling, in: Endothermic Heat-Sink Hydrocarb. Fuels Scramjet Cool., 38th
637   AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Indianapolis, Indiana, 2002: p.
638   3871.

639 [4] G. Liu, Y. Han, L. Wang, X. Zhang, Z. Mi, Supercritical thermal cracking of N -dodecane in
640   presence of several initiative additives: Products distribution and kinetics, Energy Fuels. 22
641   (2008) 3960–3969.

642 [5] K. Tabayashi, S. Bauer, The early stages of pyrolysis and oxidation of methane, Combust. Flame.
643   34 (1979) 63–83.

644 [6] S. Anderson, Breakdown behavior of fuels for pulsed detonation engines, (2005).

645 [7] T. Bruno, M. Huber, A. Laesecke, E. Lemmon, R. Perkins, Thermochemical and thermophysical
646   properties of JP-10, Adv. Sci. Tech. 45 (2006) 1–67.

647 [8] S. Garner, R. Sivaramakrishnan, K. Brezinsky, The high-pressure pyrolysis of saturated and

648 unsaturated C7 hydrocarbons, Proc. Combust. Inst. 32 (2009) 461–467.

649 [9] S. Zeppieri, S. Klotz, F. Dryer, Modeling concepts for larger carbon number alkanes: A partially

650 reduced skeletal mechanism for n-decane oxidation and pyrolysis, Proc. Combust. Inst. 28 (2000)

651 1587–1595.

652 [10] Y. Xing, W. Fang, W. Xie, Y. Guo, R. Lin, Thermal cracking of JP-10 under pressure, Ind. Eng.

653 Chem. Res. 47 (2008) 10034–10040.

654 [11] J. Chakraborty, D. Kunzru, High pressure pyrolysis of n-heptane, J. Anal. Appl. Pyrolysis. 86

655 (2009) 44–52.

656 [12] J. Dahl, V. Barocas, D. Clough, A. Weimer, Intrinsic kinetics for rapid decomposition of methane

657 in an aerosol flow reactor, Int. J. Hydrog. Energy. 27 (2002) 377–386.

658 [13] M. Khan, B. Crynes, Survey of recent methane pyrolysis literature, Ind. Eng. Chem. Res. 62

659 (1970) 54–59.

660 [14] F. Billaud, F. Baronnet, E. Freund, C. Busson, J. Weill, Thermal decomposition of methane:

661 bibliographic study and proposal of a mechanism, Rev. I. Fr. Pet. 44 (1989) 813–823.

662 [15] G. Fau, N. Gascoin, P. Gillard, J. Steelant, Methane Pyrolysis: literature survey and comparisons

663 of available data for use in numerical simulations, J. Anal. Appl. Pyrolysis. 104 (2013) 1–9.

664 [16] A. Gordon, Pyrolysis of methane flowing through a porcelain tube in the region 1000°, J. Am.

665 Chem. Soc. 70 (1948) 395–401.

666 [17] J. Weill, P. Broutin, F. Billaud, C. Guéret, Coke Formation During Hydrocarbons Pyrolysis. Part

667 One: Steam Cracking, Oil Gas Sci. Technol. 47 (1992) 537–549.

668   [18]   H. Cai, A. Krzywicki, M.C. Oballa, Coke formation in steam crackers for ethylene production,

669   Chem. Eng. Process. 41 (2002) 199–214.

670   [19]   C. Yue, A. Watkinson, J. Lucas, K. Chung, Incipient coke formation during heating of heavy

671   hydrocarbons, Fuel. 83 (2004) 1651–1658.

672   [20]   N. Gascoin, P. Gillard, S. Bernard, M. Bouchez, Characterisation of coking activity during

673   supercritical hydrocarbon pyrolysis, Fuel Process. Technol. 89 (2008) 1416–1428.

674   [21]   N. Gascoin, Coking Activity During Supercritical Hydrocarbon Pyrolysis, Hydrocarb. World. 5

675   (2010) 17–20.

676   [22]   N. Gascoin, G. Abraham, P. Gillard, Thermal and hydraulic effects of coke deposit in

677   hydrocarbon pyrolysis process., 17th AIAA Int. Sp. Planes Hypersonic Syst. Technol. Conf. 2205

678   (2011).

679   [23]   M. Bajus, V. Vesel, P. Leclercq, J. Rijks, Steam Cracking of Hydrocarbons. 1. Pyrolysis of

680   Heptane, Ind. Eng. Chem. Res. 18 (1979) 30–37.

681   [24]   G. Fau, N. Gascoin, P. Gillard, Fuel Pyrolysis through Porous Media : Coke Formation and

682   Coupled effect on Permeability, 17th AIAA Int. Sp. Planes Hypersonic Syst. Technol. Conf. 2206

683   (2011).

684   [25]   N. Gascoin, G. Abraham, P. Gillard, Thermal and Hydraulic Effects of Coke Deposit in

685   Hydrocarbon Pyrolysis Process, J. Thermophys Heat Transf. 26 (n.d.) 57–65.

686   [26]   G. Fau, N. Gascoin, P. Gillard, M. Bouchez, Fuel Pyrolysis through Porous Media: Coke

687   Formation and Coupled effect on Permeability, J. Anal. Appl. Pyrolysis. 95 (2012) 180–188.

688   [27]   M. Bouchez, E. Daniau, N. Visez, O. Herbinet, R. Fournet, P. Marquaire, Hydrocarbons

689   Heterogeneous Pyrolysis: Experiments and Modeling for Scramjet Thermal Management, 15th

690   AIAA Int. Sp. Planes Hypersonic Syst. Technol. Conf. (2009).

691   [28]   K. Davis, W. Cerven, W. Solomon, The use of methane as a fuel for hypersonic propulsion, in:

692   Use Methane as a Fuel Hypersonic Propuls., 31st AIAA/ASME/SAE/ASEE Joint Propulsion

693   Conference and Exhibit, San Diego, California, 1995: p. 2769.

694   [29]   C. Hurd, F. Pilgrim, The Pyrolysis of Hydrocarbons. Further Studies on the Butanes, J. Am.

695   Chem. Soc. 55 (1933) 4902–4907.

696   [30]   W. Slater, The influence of different surfaces on the decomposition of methane, J. Chem. Soc.

697   Trans. 109 (1916) 160–164.

698   [31]   C. Hurd, L. Eilers, Pyrolysis Studies-Isobutylene, Diisobutylene, Ethylene, Propylene, and 2-

699   Pentene, Ind. Eng. Chem. Res. 26 (1934) 776–780.

700   [32]   B. Crynes, L. Albright, Pyrolysis of propane in tubular flow reactors. Kinetics and surface effects,

701   Ind. Eng. Chem. Res. 8 (1969) 25–31.

702   [33]   M. Ghaly, B. Crynes, Reactor Surface Effects During Propylene Pyrolysis, in: Ind. Lab.

703   Pyrolyses, American Chemical Society, 1976: pp. 218–240.

704   [34]   J. Dunkleman, L. Albright, Surface Effects During Pyrolysis of Ethane in Tubular Flow Reactors,

705   in: Ind. Lab. Pyrolyses, American Chemical Society, 1976: pp. 241–260.

706   [35]   N. Gascoin, P. Gillard, S. Bernard, E. Daniau, M. Bouchez, Pyrolysis of supercritical

707   endothermic fuel: Evaluation for active cooling instrumentation, Int. J. Chem. React. Eng. 6

708   (2008).

709 [36] N. Gascoin, G. Abraham, P. Gillard, Synthetic and jet fuels pyrolysis for cooling and combustion
710 applications, J. Anal. Appl. Pyrolysis. 89 (2010) 294–306.

711 [37] G. Abraham, Etude et développement d'une méthode d'analyse par spectroscopie infrarouge
712 appliquée à la pyrolyse d'hydrocarbures en conditions supercritiques et transitoires, Ph.D. Thesis.
713 (2009).

714 [38] J. Li, J. Zou, X. Zhang, W. Guo, Z. Mi, Catalytic cracking of endothermic fuels in coated tube
715 reactor, Front. Chem. Eng. Chin. 2 (2008) 181–185.

716 [39] H. Zhao, F. Meng, W. Guo, J. Zou, X. Zhang, Pd/HZSM-5 coating catalyst for supercritical
717 cracking of endothermic fuel, J. Fuel Chem. Technol. 36 (2008) 462–467.

718 [40] F. Meng, G. Liu, S. Qu, L. Wang, X. Zhang, Z. Mi, Catalytic cracking and coking of supercritical
719 n-dodecane in microchannel coated with HZSM-5 zeolites, Ind. Eng. Chem. Res. 49 (2010)
720 8977–8983.

721 [41] Y. Xing, D. Li, W. Xie, W. Fang, Y. Guo, R. Lin, Catalytic cracking of tricyclo [5.2.1.02.6]
722 decane over HZSM-5 molecular sieves, Fuel. 89 (2010) 1422–1428.

723 [42] G. Liu, G. Zhao, F. Meng, S. Qu, L. Wang, X. Zhang, Catalytic Cracking of Supercritical n-
724 Dodecane over Wall-Coated HZSM-5 Zeolites with Micro-and Nanocrystal Sizes, Energy Fuels.
725 26 (2012) 1220–1229.

726 [43] T. Fang, C. Yeh, Catalytic pyrolysis of methane, J. Chin. Chem. Soc. 29 (1981) 265–273.

727 [44] G.P. VanDerZwet, P. Hendriks, R. VanSanten, Pyrolysis of methane and the role of surface area,
728 Catal. Today. 4 (1989) 365–369.

729 [45] M. Wolf, O. Deutschmann, F. Behrendt, J. Warnatz, Kinetic model of an oxygen-free methane
730   conversion on a platinum catalyst, Catal. Lett. 61 (1999) 15–25.

731 [46] M. Belgued, A. Amariglio, P. Paréja, Oxygen-Free Conversion of Methane to Higher Alkanes
732   through an Isothermal Two-Step Reaction on Platinum (EUROPT-1) I. Chemisorption of
733   Methane, J. Catal. 166 (1996) 118–120.

734 [47] S. Bao, G. Liu, X. Zhang, L. Wang, Z. Mi, New method of catalytic cracking of hydrocarbon
735   fuels using a highly dispersed nano-HZSM-5 catalyst, Ind. Eng. Chem. Res. 49 (2010) 3972–
736   3975.

737 [48] X. Xian, G. Liu, Z. Zhang, L. Wang, Z. Mi, Catalytic cracking of n-dodecane over HZSM-5
738   zeolite under supercritical conditions: Experiments and kinetics, Chem. Eng. Sci. 65 (2010)
739   5588–5604.

740 [49] Z. Dardas, G. Murat, Y. Ma, W. Moser, A Kinetic Study of n-Heptane Catalytic Cracking over a
741   Commercial Y-Type Zeolite under Supercritical and Subcritical Conditions, J. Catal. 162 (1996)
742   327–338.

743 [50] N. Muradov, Catalysis of methane decomposition over elemental carbon, Catal. Commun. 2
744   (2001) 89–94.

745 [51] N. Muradov, CO2-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuels for
746   transportation, Energy Fuels. 12 (1998) 41–48.

747 [52] K. Lee, G. Han, K. Yoon, B. Lee, Thermocatalytic hydrogen production from the methane in a
748   fluidized bed with activated carbon catalyst, Catal. Today. 93-95 (2004) 81–86.

749 [53] J. Pinilla, I. Suelves, M. Lázaro, R. Moliner, Kinetic study of the thermal decomposition of
750   methane using carbonaceous catalysts, Chem. Eng. J. 138 (2008) 301–306.

751 [54] Z. Bai, H. Chen, B. Li, W. Li, Catalytic decomposition of methane over activated carbon, J. Anal.
752 Appl. Pyrolysis. 73 (2005) 335–341.

753 [55] R. Moliner, I. Suelves, M. Lázaro, O. Moreno, Thermocatalytic decomposition of methane over
754 activated carbons: influence of textural properties and surface chemistry, Int. J. Hydrog. Energy.
755 30 (2005) 293–300.

756 [56] P. Ferreira-Aparicio, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Methane interaction with silica and
757 alumina supported metal catalysts, Appl. Catal. A-Gen. 148 (1997) 343–356.

758 [57] S. Takenaka, H. Ogihara, I. Yamanaka, K. Otsuka, Decomposition of methane over supported-Ni
759 catalysts: effects of the supports on the catalytic lifetime, Appl. Catal. A-Gen. 217 (2001) 101–
760 110.

761 [58] S. Zein, A. Mohamed, P. Sai, Kinetic studies on catalytic decomposition of methane to hydrogen
762 and carbon over Ni/TiO2 catalyst, Ind. Eng. Chem. Res. 43 (2004) 4864–4870.

763 [59] J. Zadeh, K. Smith, Kinetics of CH4 decomposition on supported cobalt catalysts, J. Catal. 176
764 (1998) 115–124.

765 [60] Y. Xu, L. Lin, Recent advances in methane dehydro-aromatization over transition metal ion-
766 modified zeolite catalysts under non-oxidative conditions, Appl. Catal. A-Gen. 188 (1999) 53–67.

767 [61] F. Solymosi, J. Cserenyi, A. Szöke, T. Bansagi, A. Oszko, Aromatization of methane over
768 supported and unsupported Mo-based catalysts, J. Catal. 165 (1997) 150–161.

769 [62] F. Solymosi, A. Erdöhelyi, A. Szöke, Dehydrogenation of methane on supported molybdenum
770 oxides. Formation of benzene from methane, Catal. Lett. 32 (1995) 43–53.

771   [63]   F. Solymosi, A. Szöke, J. Cserenyi, Conversion of methane to benzene over Mo2C and

772   Mo2C/ZSM-5 catalysts, Catal. Lett. 39 (1996) 157–161.

773   [64]   J. Lunsford, Catalytic conversion of methane to more useful chemicals and fuels: a challenge for

774   the 21st century, Catal. Today. 63 (2000) 165–174.

775   [65]   A. Holmen, Direct conversion of methane to fuels and chemicals, Catal. Today. 142 (2009) 2–8.

776   [66]   N. Shah, D. Panjala, G. Huffman, Hydrogen production via catalytic decomposition of methane,

777   Energy & Fuels. 15 (2001) 1528–1534.

778   [67]   I. González, J. De Jesus, C. De Navarro, M. Garcia, Effect of Cu on Ni nanoparticles used for the

779   generation of carbon nanotubes by catalytic cracking of methane, Catal. Today. 149 (2010) 352–

780   357.

781   [68]   A. Amin, E. Croiset, W. Epling, Review of methane catalytic cracking for hydrogen production,

782   Int. J. Hydrog. Energy. (2011) 1–32.

783   [69]   S. Ahmed, A. Aitani, F. Rahman, A. Al-Dawood, F. Al-Muhaish, Decomposition of

784   hydrocarbons to hydrogen and carbon, Appl. Catal. A-Gen. 359 (2009) 1–24.

785   [70]   H. Abbas, W. Wan Daud, Hydrogen production by methane decomposition: a review, Int. J.

786   Hydrog. Energy. 35 (2010) 1160–1190.

787   [71]   L. Albright, C. McConnell, K. Welther, Types of coke formed during the pyrolysis of light

788   hydrocarbons, in: Therm. Hydrocarb. Chem., Purdue Univ., West Lafayette, IN, 1979: pp. 175–

789   191.

790   [72]   E. Fitzer, K. Kochling, H. Boehm, H. Marsh, Recommended terminology for the description of

791   carbon as a solid, Pure Appl. Chem. 67 (1995) 473–506.

792   [73]   T. Edwards, S. Zabarnick, Supercritical fuel deposition mechanisms, Ind. Eng. Chem. Res. 32
793   (1993) 3117–3122.

794   [74]   W. Xie, W. Fang, D. Li, Y. Xing, Y. Guo, R. Lin, Coking of model hydrocarbon fuels under
795   supercritical condition, Energy Fuels. 23 (2009) 2997–3001.

796   [75]   A. Baiker, Supercritical fluids in heterogeneous catalysis, Chem. Rev. 99 (1999) 453–474.

797   [76]   E. Blekkan, R. Myrstad, O. Olsvik, O. Rokstad, Characterization of tars and coke formed during
798   the pyrolysis of methane in a tubular reactor, Carbon N. Y. 30 (1992) 665–673.

799   [77]   C. Guéret, F. Billaud, B. Fixari, P. Le Perchec, Thermal coupling of methane, experimental
800   investigations on coke deposits, Carbon N. Y. 33 (1995) 159–170.

801   [78]   L. Albright, J. Marek, Coke formation during pyrolysis: Roles of residence time, reactor
802   geometry, and time of operation, Ind. Eng. Chem. Res. 27 (1988) 743–751.

803   [79]   O. Altin, S. Eser, Characterization of carbon deposits from jet fuel on Inconel 600 and Inconel X
804   surfaces, Ind. Eng. Chem. Res. 39 (2000) 642–645.

805   [80]   O. Altin, E. Semih, Analysis of solid deposits from thermal stressing of a JP-8 fuel on different
806   tube surfaces in a flow reactor, Ind. Eng. Chem. Res. 40 (2001) 596–603.

807   [81]   G. Reyniers, G. Froment, F. Kopinke, G. Zimmermann, Coke formation in the thermal cracking
808   of hydrocarbons. 4. Modeling of coke formation in naphtha cracking, Ind. Eng. Chem. Res. 33
809   (1994) 2584–2590.

810   [82]   P. Lucas, A. Marchand, Pyrolytic carbon deposition from methane: an analytical approach to the
811   chemical process, Carbon N. Y. 28 (1990) 207–219.

812   [83]   A. Oberlin, Pyrocarbons, Carbon N. Y. 40 (2002) 7–24.

813 [84] O. Altin, S. Eser, Analysis of carboneceous deposits from thermal stressing of a JP-8 fuel on
814   superalloy foils in a flow reactor, Ind. Eng. Chem. Res. 40 (2001) 589–595.

815 [85] A. Radwan, T. Kyotani, A. Tomita, Characterization of coke deposited from cracking of benzene
816   over USY zeolite catalyst, Appl. Catal. A-Gen. 192 (2000) 43–50.

817 [86] A. Shamsi, J. Baltrus, J. Spivey, Characterization of coke deposited on Pt/alumina catalyst during
818   reforming of liquid hydrocarbons, Appl. Catal. A-Gen. 293 (2005) 145–152.

819 [87] W. Zhiyuan, X. Hong, L. Xiaojian, H. Feng, Z. Jianxin, Effect of Potassium Acetate on Coke
820   Growth during Light Naphtha Thermal Cracking, Ind. Eng. Chem. Res. 50 (2011) 10292–10297.

821 [88] E. Furimsky, Characterization of cokes from fluid/flexi-coking of heavy feeds, Fuel Process.
822   Technol. 67 (2000) 205–230.

823 [89] H. Schobert, C. Eser, C. Song, P. Hatcher, A. Boehman, M. Coleman, Advanced thermally stable
824   jet fuels, 1996.

825 [90] M. Guisnet, P. Magnoux, Organic chemistry of coke formation, Appl. Catal. A-Gen. 212 (2001)
826   83–96.

827 [91] W. Benzinger, A. Becker, K. Hüttinger, Chemistry and kinetics of chemical vapour deposition of
828   pyrocarbon: I. Fundamentals of kinetics and chemical reaction engineering, Carbon N. Y. 34
829   (1996) 957–966.

830 [92] A. Becker, K. Hüttinger, Chemistry and kinetics of chemical vapor deposition of pyrocarbon–IV
831   pyrocarbon deposition from methane in the low temperature regime, Carbon N. Y. 36 (1998)
832   213–224.

833   [93]   L. Albright, J. Marek, Mechanistic model for formation of coke in pyrolysis units producing
834   ethylene, Ind. Eng. Chem. Res. 27 (1988) 755–759.

835   [94]   H. Böhm, H. Jander, D. Tanke, PAH growth and soot formation in the pyrolysis of acetylene and
836   benzene at high temperatures and pressures: Modeling and experiment, Symp. (Int.) Combust. 27
837   (1998) 1605–1612.

838   [95]   H. Böhm, H. Jander, PAH formation in acetylene–benzene pyrolysis, Phys. Chem. Chem. Phys. 1
839   (1999) 3775–3781.

840   [96]   P. Vlasov, J. Warnatz, Detailed kinetic modeling of soot formation in hydrocarbon pyrolysis
841   behind shock waves, Proc. Combust. Inst. 29 (2002) 2335–2341.

842   [97]   G. Agafonov, I. Naydenova, P. Vlasov, J. Warnatz, Detailed kinetic modeling of soot formation
843   in shock tube pyrolysis and oxidation of toluene and n-heptane, Proc. Combust. Inst. 31 (2007)
844   575–583.

845   [98]   R. Terry, K. Baker, Coking problems associated with hydrocarbon conversion processes, Prepr.
846   Pap. Am. Chem. Soc. Div. Fuel Chem. 41 (1996) 521–524.

847   [99]   R. Baker, M. Barber, P. Harris, R. Waite, Nucleation and growth of carbon deposits from the
848   nickel catalyzed decomposition of acetylene, J. Catal. 62 (1972) 51–62.

849   [100] J. Rostrup-Nielsen, D. Trimm, Mechanisms of carbon formation on nickel-containing catalysts, J.
850   Catal. 48 (1977) 155–165.

851   [101] J. Butt, R. Billimoria, Catalyst Deactivation, in: Chem. React. Eng. Rev., American Chemical
852   Society, 1978: pp. 288–322.

853   [102] D. Trimm, Catalyst design for reduced coking (review), Appl. Catal. 5 (1983) 263–290.

854 [103] C. Bartholomew, Mechanisms of catalyst deactivation, Appl. Catal. A-Gen. 212 (2001) 17–60.

855 [104] M. Guisnet, P. Magnoux, Coking and deactivation of zeolites: Influence of the Pore Structure,
856   Appl. Catal. 54 (1989) 1–27.

857 [105] P. Magnoux, M. Guisnet, Coking, aging, and regeneration of zeolites: X-nature of coke formed
858   on H-erionite during n-heptane cracking, mode of deactivation, Zeolites. 9 (1989) 329–335.

859 [106] M. Guisnet, P. Magnoux, Deactivation by coking of zeolite catalysts. Prevention of deactivation.
860   Optimal conditions for regeneration, Catal. Today. 36 (1997) 477–483.

861 [107] B. Paweewan, P. Barrie, L. Gladden, Coking and deactivation during n-hexane cracking in
862   ultrastable zeolite Y, Appl. Catal. A-Gen. 185 (1999) 259–268.

863 [108] R. De Pauw, G. Froment, Deactivation of a platinum reforming catalyst in a tubular reactor,
864   Chem. Eng. Sci. 30 (1975) 789–801.

865 [109] J. Beeckmann, G. Froment, P. L, Deactivation of porous catalysts by coke formation, Chem. Ing.
866   Tech. 12 (1978) 960–961.

867 [110] J. Beeckman, G. Froment, Catalyst deactivation by active site coverage and pore blockage, Ind.
868   Eng. Chem. Fundam. 18 (1979) 245–256.

869 [111] J. Beeckman, G. Froment, Catalyst deactivation by site coverage and pore blockage: Finite rate of
870   growth of the carbonaceous deposit, Chem. Eng. Sci. 35 (1980) 805–815.

871 [112] J. Beeckman, G. Froment, Deactivation of catalysts by coke formation in the presence of internal
872   diffusional limitation, Ind. Eng. Chem. Fundam. 21 (1982) 243–250.

873 [113] G. Marin, J. Beeckman, G. Froment, Rigorous kinetic models for catalyst deactivation by coke
874   deposition: Application to butene dehydrogenation, J. Catal. 426 (1986) 416–426.

875   [114] I. Nam, G. Froment, Catalyst deactivation by site coverage through multi-site reaction

876   mechanisms, J. Catal. 108 (1987) 271–282.

877   [115] G. Froment, J. Meyer, E. Derouane, Deactivation of zeolite catalysts by coke formation, J. Catal.

878   124 (1990) 391–400.

879   [116] G. Froment, Modeling of catalyst deactivation, Appl. Catal. A-Gen. 212 (2001) 117–128.

880   [117] J. Beltramini, T. Wessel, D. Ravindra, Kinetics of deactivation of bifunctional Pt/Al2O3-Cl

881   catalysts by coking, AIChE J. 37 (1991) 845–854.

882   [118] W. Groten, B. Wojciechowski, B. Hunter, On the relationship between coke formation chemistry

883   and catalyst deactivation, J. Catal. 138 (1992) 343–350.

884   [119] P. Forzatti, L. Lietti, Catalyst deactivation, Catal. Today. 52 (1999) 165–181.

885   [120] M. Reyniers, H. Beirnaert, G. Marin, Influence of coke formation on the conversion of

886   hydrocarbons I. Alkanes on a USY-zeolite, Appl. Catal. A-Gen. 202 (2000) 49–63.

887   [121] M. Reyniers, Y. Tang, G. Marin, Influence of coke formation on the conversion of hydrocarbons:

888   II. i-Butene on HY-zeolites, Appl. Catal. A-Gen. 202 (2000) 65–80.

889   [122] A. Mohamadalizadeh, J. Towfighi, R. Karimzadeh, Modeling of catalytic coke formation in

890   thermal cracking reactors, J. Anal. Appl. Pyrolysis. 82 (2008) 134–139.

891