

1 Alumina Supported Iron Catalysts for the Selective
2 Acetylene Hydrogenation under Industrial Front-End
3 Conditions[†]

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13

14 ABSTRACT:

15 The removal of acetylene traces from ethylene streams coming from the steam cracker is carried
16 out in the industry on an annual scale of several million tonnes using Pd-Ag/Al₂O₃ catalysts. The
17 substitution of palladium containing catalysts with more abundant, cheap and non-toxic materials
18 is a first crucial step towards a more sustainable chemical industry. Since iron is one of the most
19 abundant metals and can be mined in almost all regions world wide, it is an ideal catalyst material.
20 In this work, we present the development of alpha alumina supported iron catalysts with 1 wt%,
21 5 wt% and 10 wt% iron loading and their application in the selective acetylene hydrogenation
22 under industrially applied front-end conditions. The catalysts were prepared via simple incipient
23 wetness impregnation and were analyzed via XRD, XRF, TPR, TEM and N₂-Physisorption. The
24 catalysts were subsequently calcined, reduced and tested in the selective acetylene hydrogenation.
25 After an activation phase, the catalysts show excellent activity and selectivity in the acetylene
26 hydrogenation at 90 °C without significant ethylene hydrogenation. The excellent catalytic activity
27 underline the great potential of iron based catalysts as an alternative to conventional Pd-containing
28 materials.

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31 KEYWORDS: *Heterogenous Catalysis, Acetylene Hydrogenation, Front-End Conditions,*
32 *Semihydrogenation, Supported Iron nanoparticles.*

33

34 **1 Introduction**

35 Ethylene is one of the most important platform chemicals due to its application as monomer in
36 polymer production and as reactant for the production of intermediate products such as
37 dichloroethane, ethylene oxide, ethyl benzene and vinyl acetate.^[1,2] The conventional route for the
38 production of ethylene is the cracking of naphta or recently, the production from bioethanol by
39 dehydration. The cracking conditions mainly favour the formation of olefins as well as the
40 formation of smaller amounts of multi unsaturated compounds.^[1] High purity ethylene streams are
41 required especially in polymer production to ensure reproducible product qualities. Multi-
42 unsaturated impurities such as acetylene lead to poisoning of Ziegler-Natta catalysts in
43 polymerization reactions.^[3-5] Therefore, the generation of ethylene-rich streams with acetylene
44 concentrations lower than 1 ppm are necessary.^[3-7]

45 Industrially, two main operating methods are commonly used for acetylene removal, tail-end and
46 front-end operation. In the first case, the acetylene removal unit is located after the de-ethanizer.
47 The feed contains only C₂-fractions and stoichiometrically added hydrogen.^[6-10] The low hydrogen
48 concentration guarantees a high selectivity for conversion of acetylene to ethylene avoiding the
49 overhydrogenation to ethane. However, it favors increased oligomer and green oil formation
50 leading to shorter catalyst lifetimes in the acetylene hydrogenation. Due to the lower risk of reactor
51 runaway, hydrogenation under tail-end conditions is most widely used in industry and well
52 researched.^[7,10-12] The hydrogenation under front-end conditions takes place in front of the
53 demethanizer^[8] and therefore, the feed contains high hydrogen concentration as well as carbon
54 monoxide and methane.^[3,4,6,10,12,13] This carries the risk of overhydrogenation and hot spot
55 formation.^[4] The key advantage of front-end conditions is the improved process integration

56 combined with longer catalyst life cycles and has been studied intensively in the recent years.^{[4,13-}
57 ^{15]}

58 State of the art catalysts for both operation modes are palladium based catalyst systems.^[4,6,7,12]

59 Owing to the low availability of palladium, its mining process consumes large amounts of fresh
60 water^[16] and has a low atom economy,^[16,17] while producing high amounts of carbon dioxide^[18,19]
61 due to high electricity consumption.^[16,17,19] It is therefore important to reduce or substitute the use
62 of this critical raw material. In order to reduce the amount of palladium required and increase the
63 selectivity of the acetylene hydrogenation reaction, palladium single-atom catalysts^[20,21] and
64 palladium single sites incorporated into bimetallic systems have been the focus of recent research
65 in this field. Some examples of bimetallic materials are PdAg^[22–26], PdAu,^[22,25,27,28] PdIn,^[29]
66 PdGa^[22,30,31] as well as PdCu^[22,32] and PdZn^[5,20,22,33] compounds and the incorporation of Pd into
67 metal-organic frameworks (MOF).^[34]

68 The substitution of palladium by more abundant metals as active species is even more favorable.
69 Therefore, intermetallic phases and alloys of bi- and trimetallic palladium-free catalyst systems
70 such as supported AuAg^[35], AgNi^[36] and NiIn^[37] systems as well as Cu-Ni-Fe systems^[38] have
71 been tested and show high activity and selectivity in the acetylene hydrogenation. Studt et al.
72 performed DFT calculations to identify non-precious metal alloys as catalysts for selective
73 acetylene hydrogenation.^[39] They predicted and confirmed the suitability of NiZn and NiZn₃ as
74 well as FeZn alloys as catalysts with high selectivity and activity.^[39]

75 A promising way to replace palladium as catalyst is the use of pure iron catalysts for the selective
76 acetylene hydrogenation. Zero-valent iron as well as Fe^{II} and Fe^{III} are known for their
77 hydrogenation activity.^[40–45] Furthermore, iron is one of the most abundant metals resulting in a
78 low carbon footprint and low water consumption during its production.^[17]

79 Tejada-Serrano et al. published the application of a Fe^{III}-O metal-organic framework as catalyst
80 for the acetylene hydrogenation under front-end conditions.^[45] The iron-based MOF reduces the
81 acetylene content from 1.2 % to less than 10 ppm at 150 °C while ethane formation remains below
82 10 %. The increase of ethane formation over time indicates degradation of the catalyst under
83 reaction conditions.^[45]

84 More recently, Hock et al. published zero-valent iron nanoparticles as a very promising catalyst
85 under front-end conditions.^[15] The catalyst shows good activity of 14 % acetylene conversion at
86 90 °C and excellent selectivity. In addition, the selectivity could be improved by adding carbon
87 monoxide as selectivity directing agent.^[15]

88 Based on these results, the systematic investigation and optimization of the catalytic properties of
89 the above mentioned iron nanoparticles is of interest. Therefore, we developed supported iron
90 nanoparticles with different iron loadings as catalysts for the selective acetylene hydrogenation
91 under industrially relevant front-end conditions. This results in catalysts with smaller iron particle
92 sizes, higher surface area and improved dispersion, leading to catalysts with excellent performance
93 and selectivity.

94 **2 Experimental**

95 **2.1 Materials**

96 Hydrogen (H₂, N50), methane (CH₄, N25), ethylene (C₂H₄, N35), an acetylene/propane/methane-
97 mixture (1.2 mol% C₂H₂, 1 mol% C₃H₈, N25, remaining CH₄, N25) and argon (Ar, N50) were
98 purchased from Air Liquide. Iron(III) nitrate nonahydrate (Fe(NO₃)₃ · 9 H₂O, 99 %) was purchased
99 from Acros Organics, aluminum oxide (α-Al₂O₃, 99.95 %) from thermo scientific and
100 iron(III)oxide (Fe₂O₃, 96 %) from Sigma-Aldrich. All materials were used as purchased.

101 **2.2 Synthesis of supported Iron Nanoparticles**

102 The synthesis of supported iron nanoparticles was carried out via incipient wetness impregnation.
103 Catalysts with iron loadings of 1 wt%, 5 wt%, and 10 wt% were synthesized. The respective
104 quantities of iron nitrate nonahydrate were dissolved in the volume of water corresponding to that
105 of the pores in the alpha-alumina support. The pore volume of aluminum oxide was determined
106 through N₂ physisorption. Subsequently, the iron nitrate solution was added dropwise to the
107 support, was mixed until a homogeneous paste was obtained and was treated in an ultrasonic bath
108 for 30 minutes. The paste was dried over night in a vacuum oven at 60 °C. Due to the low pore
109 volume and surface area of α -Al₂O₃, the impregnation resulted in inhomogeneous distribution of
110 iron nitrate as a crust on the surface. Therefore, the impregnated catalyst was mortared in acetone
111 till all liquid is evaporated to ensure that the Fe-species is homogeneously distributed. The dried
112 impregnated catalyst was then calcined in air at 600 °C for four hours (ramp: 5 °C min⁻¹, 100 mL
113 min⁻¹ Air). Right before the catalytic testing, the catalyst was reduced in hydrogen at 900 °C for
114 three hours (ramp: 10 °C min⁻¹, 100 mL min⁻¹ H₂).

115 **2.3 Catalyst Characterization**

116 The catalysts were analyzed with X-ray diffraction, X-ray fluorescence, temperature-programmed
117 reduction, N₂-physisorption and TEM. Detailed information regarding the measurement protocol
118 of each method can be found in the supporting information.

119 **2.4 Selective semi-hydrogenation of Acetylene**

120 A continuously operated fixed-bed reactor is used for the catalytic testing of the iron-based
121 catalysts. A filter frit with a pore size of 5 μ m is inserted into the tubular reactor to position the
122 powdered catalyst. Prior to the reaction, the reduced catalyst was removed from the reduction

123 furnace, exposed to air and 200 mg of catalyst was weighed into the tubular reactor. In each
124 experiment the temperature was varied between 30 °C and 90 °C at 22.5 bar. The feed composition
125 corresponds to that of an acetylene removal unit (ARU) under front-end conditions (Table 1). A
126 scheme of the experimental setup is included in the supporting information (Figure S4).

127 *Table 1: Feed composition and flow rate applied to all experiments.^[4]*

Flow	12.5 L h ⁻¹
x(C₂H₂)	0.4 mol%
x(C₂H₄)	39 mol%
x(H₂)	25 mol%
x(C₃H₈)_{standard}	0.34 mol%
x(CH₄)	35.26 mol%

128
129 The feed composition was realized by adding the different gas mixtures listed in chapter 2.1
130 through mass flow controllers. The composition of the output was monitored via GC with a FID
131 analyzer. Detailed Information regarding the GC Method and the column can be found in the
132 supporting information (GC program, Table S1). In each experiment the temperature is varied
133 from 30 to 90 °C in 10 °C steps. Every temperature step was held for 100 min.

134 **3 Results and discussion**

135 The synthesized supported iron nanoparticles were analyzed by XRD, XRF, N₂-physisorption,
136 TEM and TPR measurements. The catalyst with 1 wt%, 5 wt% and 10 wt% iron loading were
137 tested as catalysts in the acetylene hydrogenation under industrial relevant front-end conditions.

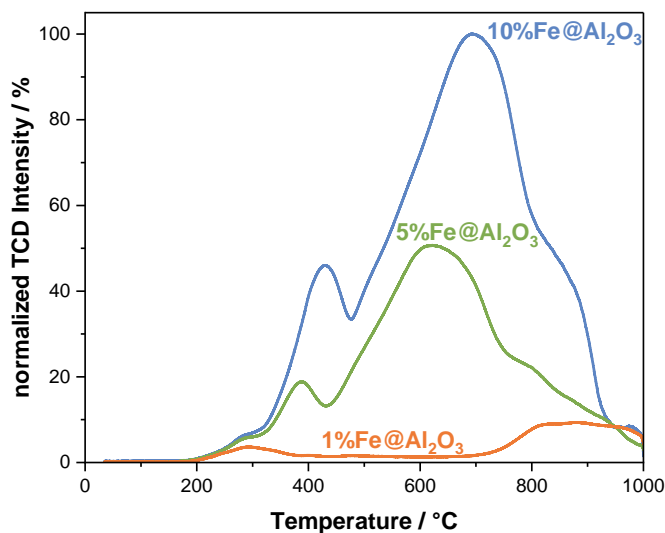
138 3.1 Synthesis and Characterization

139 The catalysts with 1 wt%, 5 wt% and 10 wt% iron loading supported on α -Al₂O₃ were synthesized
140 by incipient wetness impregnation using water and acetone as solvents. The catalyst precursors
141 were calcined at 600 °C. The iron loadings of the resulting iron oxides on α -Al₂O₃ were determined
142 by X-ray fluorescence using a calibration (Figure S1). The actual values were close to the target
143 values, indicating a successful synthesis (Figure S2). Immediately prior to catalytic testing, the
144 solids were reduced in hydrogen atmosphere at 900 °C. The reduction temperature was determined
145 by TPR. The reduction profile of the supported iron oxides with 1 wt%, 5 wt% and 10 wt% iron
146 loading showed the reduction pathway from Fe₂O₃ to Fe⁰ for different iron loadings. It is reported
147 in the literature, that the reduction of supported Fe₂O₃ in hydrogen atmosphere follows a two-step
148 reduction:^[46]



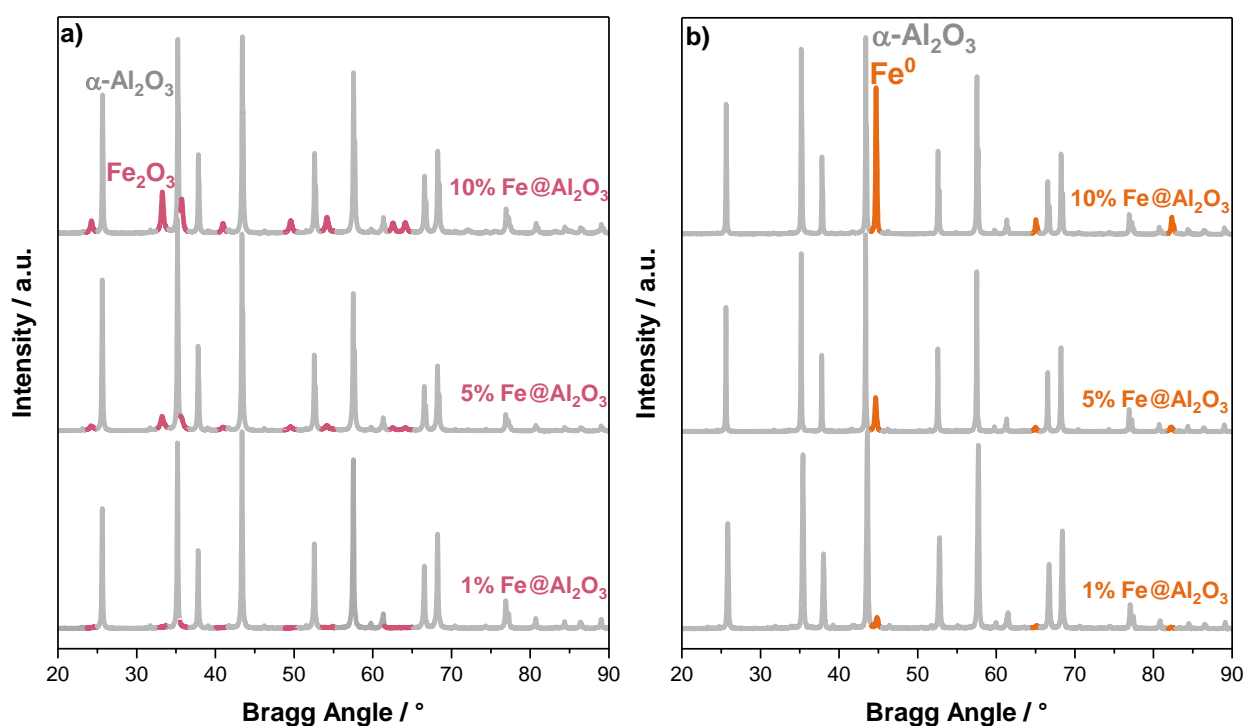
151 The TPR patterns (Figure 1) show two distinct peaks. The catalysts with higher iron loading of
152 5 wt% and 10 wt% show peaks at about 400 °C and between 630 and 700 °C. The first peak
153 indicates the reduction of Fe₂O₃ to Fe₃O₄. Fe₃O₄ is further reduced to Fe⁰ at the second peak. The
154 peak intensities correlate with the hydrogen consumption for each reduction step and the iron
155 loading. For supported catalysts, the interaction between the metal particles and the support at high
156 temperatures is reported.^[47] The peak shoulder at about 800 °C indicates the formation of iron
157 aluminates. The peaks are shifted for the catalyst with 1 wt% iron loading. The reduction of Fe₂O₃
158 to Fe₃O₄ occurs at lower temperatures of around 300 °C while the reduction to Fe⁰ is shifted to
159 significantly higher temperatures between 800 °C and 1000 °C. In addition, a peak broadening
160 occurs at high temperatures. The peak broadening and the high reduction temperature are related

161 to small particle sizes at lower loadings and stronger interactions between the Fe particles and the
162 support favoring the formation of iron aluminates. To ensure complete reduction of the iron
163 catalysts and to maintain the same reduction procedure in all three cases, the reduction temperature
164 was set to 900 °C.
165



166
167 *Figure 1: TPR pattern of the catalysts with 1 wt%, 5 wt% and 10 wt% iron loading between 30 °C and 1000 °C.*
168

169 Figure 2 shows the diffraction pattern of the catalysts a) after calcination and b) after reduction.
 170 The calcined catalyst (a) shows α - Al_2O_3 reflexes (gray)^[48] and Fe_2O_3 reflexes (red)^[49] with lower
 171 intensity. The intensity of Fe_2O_3 reflexes increases with increasing Fe loading. No other iron oxide
 172 species were observed. After reduction at 900 °C all Fe_2O_3 reflexes disappear and the diffraction
 173 pattern of Fe^0 becomes visible (orange),^[50,51] indicating complete reduction. The reflexes of Fe_2O_3 ,
 174 α - Al_2O_3 as well as Fe^0 are in good agreement with literature data.^[50,51,48,49]
 175



176
 177 *Figure 2:* a) XRD measurements of the calcined catalysts with 1 wt%, 5 wt% and 10 wt% Fe-Loading. b) XRD measurements of
 178 the reduced catalysts with 1 wt%, 5 wt% and 10 wt% Fe-Loading.

179
 180 The crystallite size of iron oxide and Fe^0 nanoparticles on alpha alumina support was determined
 181 using the Scherrer equation. To calculate the crystallite size of Fe_2O_3 , the Scherrer equation was
 182 applied for the (211) reflexes at $23^\circ 2\theta$, the (222) reflexes at $32.5^\circ 2\theta$, the (510) reflexes at 48.5°
 183 2θ and the (440) reflexes at $54.5^\circ 2\theta$. The crystallite size of Fe^0 for the reduced iron catalysts was

184 determined analogously using the (110) reflexes at $44.5^\circ 2\theta$, the (200) reflexes at $65^\circ 2\theta$ and the
185 (211) reflexes at $82.5^\circ 2\theta$. The average crystallite size of all reflections of Fe_2O_3 and Fe^0 for 1 wt%,
186 5 wt% and 10 wt% iron loading are shown in Table 2. The crystallite size of the reduced iron
187 particles increases in comparison to the Fe_2O_3 particles due to the high reduction
188 temperature of 900°C indicating sintering. The crystalite sizes for the alpha alumina support is
189 added to the supporting information.

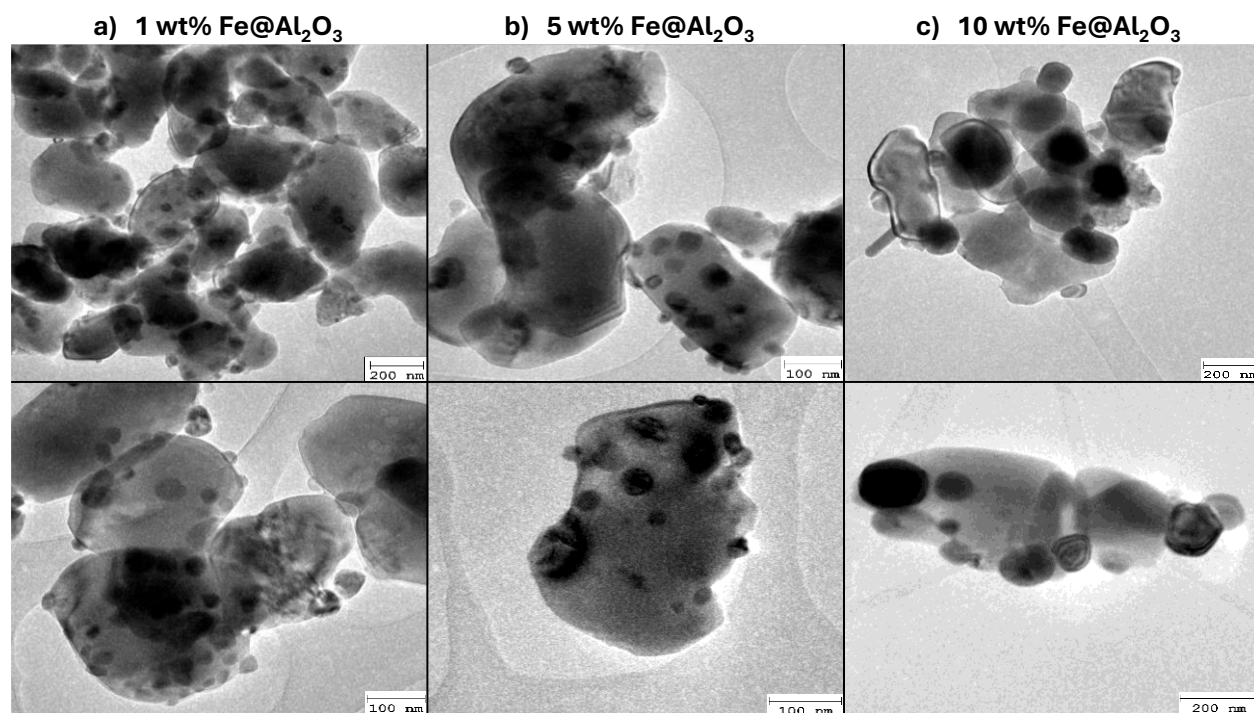
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191 *Table 2: Crystallite sizes of the unreduced and reduced catalysts with 1 wt%, 5 wt% and 10 wt% iron loading.*

	Crystalite size (calc. cat.) / nm	Std. dev / nm	Cryststalite size (red. cat.) / nm	Std. dev / nm
1 wt% Fe@Al₂O₃	-	-	26.6	0
5 wt% Fe@Al₂O₃	20.0	1.4	31.2	2.4
10 wt% Fe@Al₂O₃	25.2	1.2	48.7	4.2

192

193 Transmission electron microscopy was used to identify the iron dispersion and the size of the
194 reduced iron nanoparticles (Figure 3).



195

196 *Figure 3: TEM images of the reduced catalysts with a) 1 wt% iron loading, b) 5 wt% iron loading and c) 10 wt% iron loading.*

197

198 The TEM images show that the iron nanoparticles (darker spots) are deposited on the surface of
 199 the α -alumina support (brighter particles). As the loading increases, the size of the nanoparticles
 200 increases. Lower iron loadings lead to higher interaction between the support and the iron as well
 201 as to a higher dispersion.

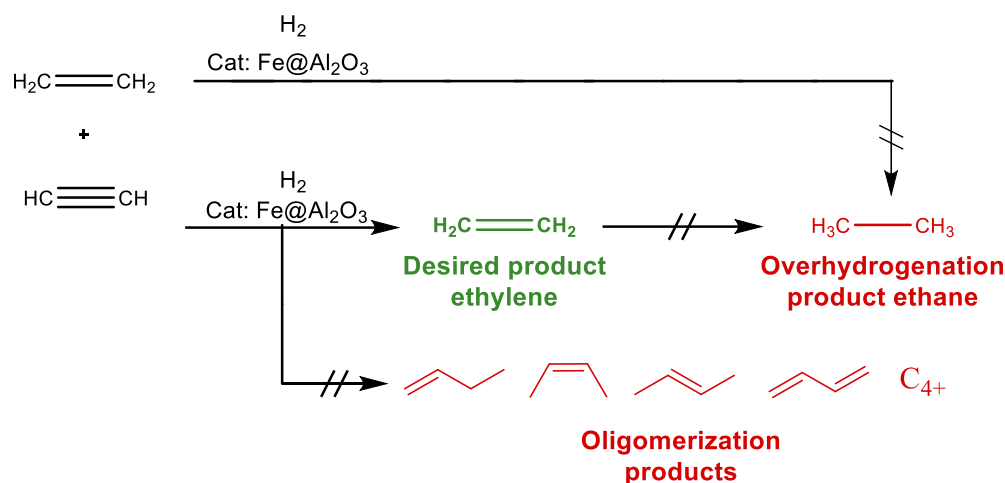
202 N_2 -physisorption measurements of the unreduced catalysts show that the impregnation of iron has
 203 no significant effect on the specific surface area compared to pure aluminum oxide (Figure S3).

204

205 **3.2 Acetylene Hydrogenation**

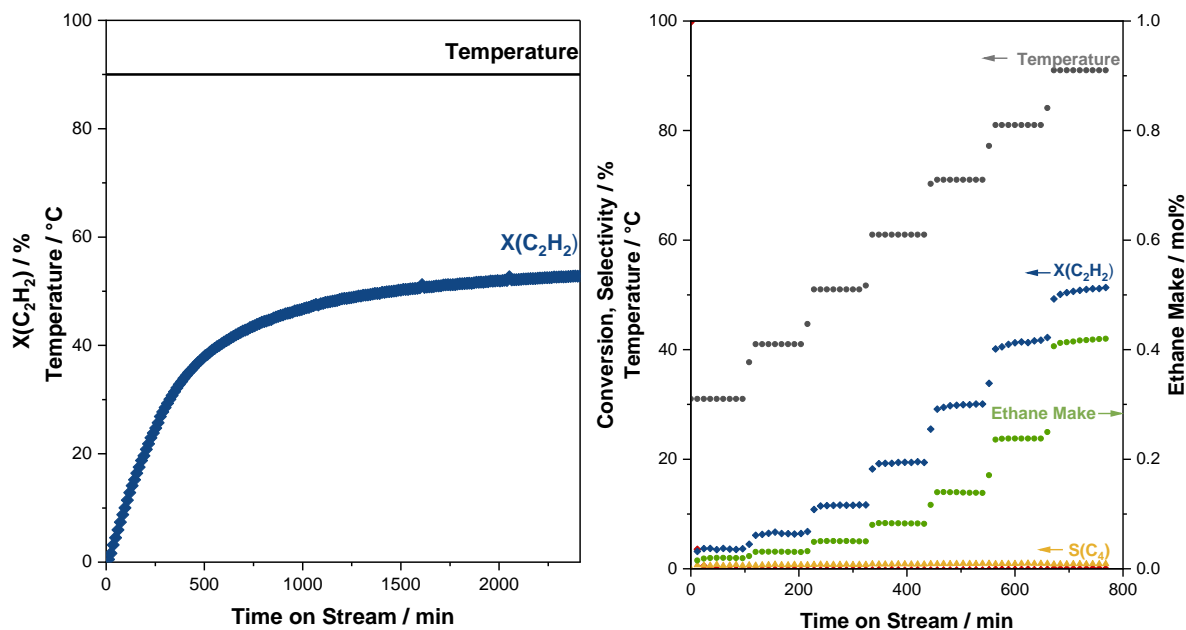
206 Catalytic tests of the above mentioned catalysts with 1 wt%, 5 wt% and 10 wt% Fe loading were
 207 carried out in a fixed bed reactor at temperatures between 30 °C and 90 °C and a pressure of
 208 22.5 bar aiming to model industrial front-end conditions of an acetylene removal unit.^[4] The feed

209 composition is given in Table 1. The observed product spectrum and the reaction pathways are
 210 shown below (Scheme 1). In general, catalysts with low selectivity towards ethane and the
 211 oligomerization products are suitable for the acetylene hydrogenation.
 212



213
 214 *Scheme 1: Reaction scheme for the acetylene hydrogenation under front-end conditions including the desired product ethylene, the*
 215 *undesired overhydrogenation product ethane and the oligomerization products Z-butene, E-butene, 1-butene, butadiene, and*
 216 *higher oligomerization products C₄₊.*

217
 218 Prior to the catalytic testing in the acetylene hydrogenation, the catalysts were reduced at 900 °C
 219 and transferred to the reactor as quickly as possible. At 90 °C under constant reaction conditions,
 220 the activation of each catalyst was observed at the beginning of the catalytic test (Figure 4, left).
 221 The activity shows a steep increase and reaches a plateau after 40 h time on stream. Afterwards,
 222 the temperature was varied between 30 °C and 90 °C in 10 °C steps, with stable activity and
 223 selectivity for each temperature (Figure 4, right).



224

225 *Figure 4: Left: Activation behavior, conversion of acetylene under reaction conditions at 90 °C exemplarily shown for the catalyst*
 226 *with 5 wt% iron loading in the first 40 h time on stream. Right: Acetylene (blue) and ethylene (red) conversion as well as C₄-*
 227 *selectivity (yellow) and ethane make (green) for the 5 wt%Fe@Al₂O₃ catalyst after the activation phase.*

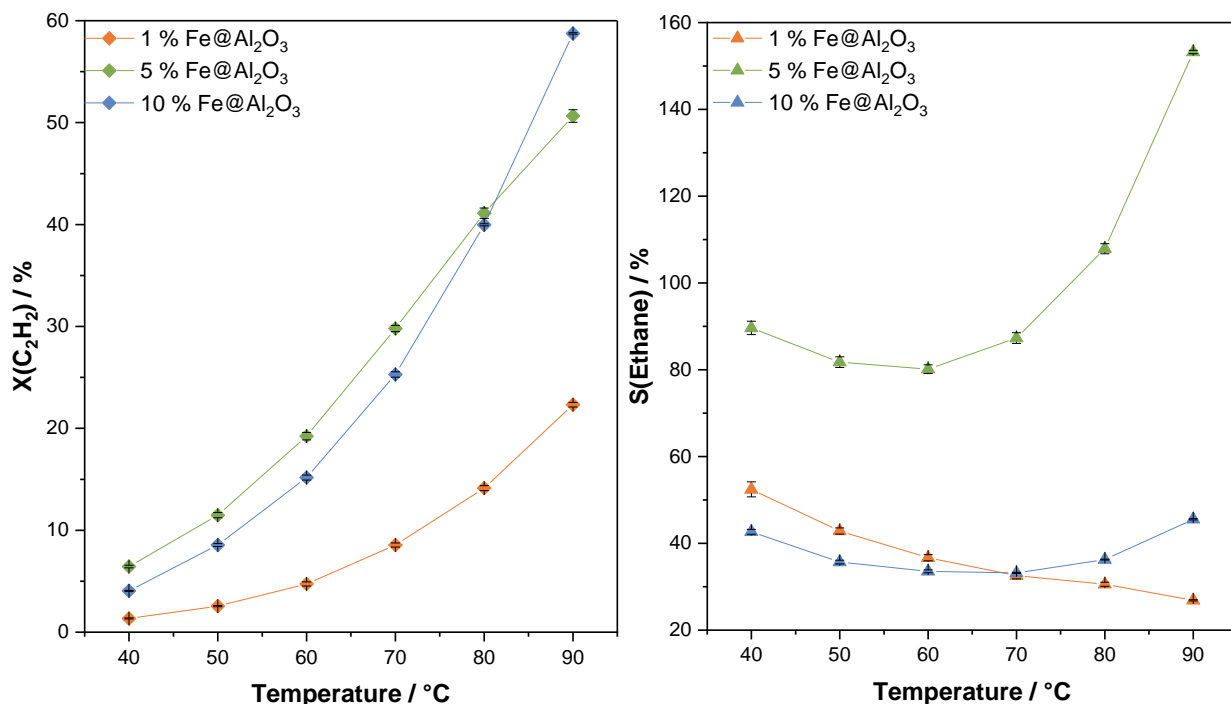
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229 The increase in activity with time at constant temperature and feed composition might indicate the
 230 reduction of remaining oxidic species on the surface and the formation of the active species under
 231 reaction conditions. The oxidic species originates from contact with air as the reduced catalyst is
 232 transferred from the reduction furnace to the reactor. The reducing reaction conditions seem to be
 233 able to reduce the catalyst surface in situ at 90 °C. Therefore, the synthesized catalysts with 1 wt%,
 234 5 wt% and 10 wt% iron loading were tested in the acetylene hydrogenation following the same
 235 reaction protocol:

- 236 1) Catalyst treated at 90 °C for 40 h under reaction conditions (Table 1)
 237 2) Cooling to 40 °C in methane atmosphere
 238 3) Heating under reaction conditions in 10 °C steps from 40 to 90 °C with a heating ramp of
 239 1 °C per minute and detection of the conversions and selectivities via GC

240 The acetylene conversion and the ethane selectivity of the different catalysts after the activation
241 phase between 30 °C and 90 °C are shown in Figure 5.

242



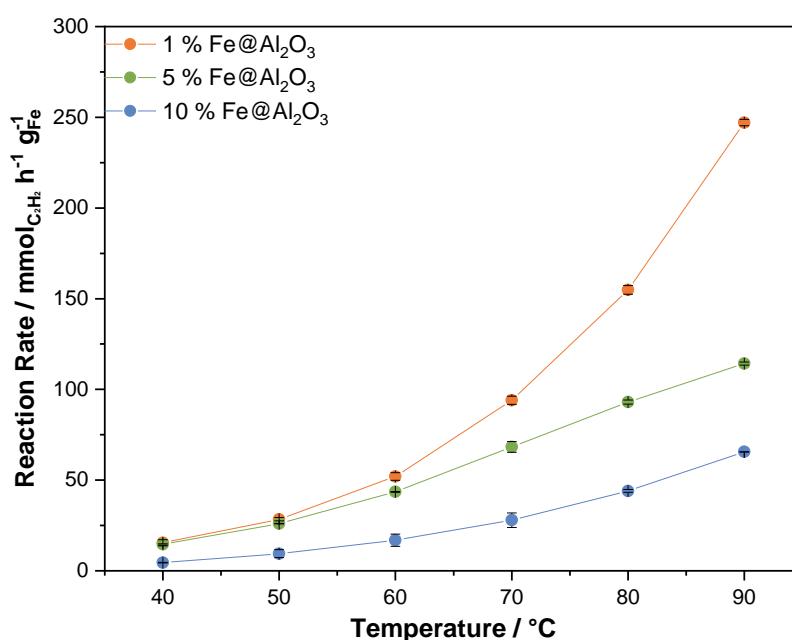
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244 *Figure 5: Left: Acetylene conversions between 30 °C and 90 °C for the catalysts with 1 wt% (orange), 5 wt% (green) and 10 wt%*
245 *(blue) iron loading. Right: Ethane make between 30 °C and 90 °C for the catalysts with 1 wt% (orange), 5 wt% (green) and 10 wt%*
246 *(blue) iron loading.*

247

248 The acetylene conversion of the catalysts (Figure 5, left) with 1 wt%, 5 wt% and 10 wt% iron
249 loading increases with increasing temperature, while the activity of the catalyst with 5 wt% and
250 10 wt% iron loading shows the highest activity. The catalyst with 5 wt% iron loading shows the
251 highest activity at lower temperatures. The activity of the catalyst with 10 wt% iron loading exceeds
252 its activity only at 90 °C. When looking at the selectivity to ethane (Figure 5, right), values above
253 100 % were obtained. This is due to the fact that the ethane selectivity was calculated based on the
254 acetylene conversion. Since ethane can also be formed by hydrogenation of ethylene, ethane
255 selectivities above 100 % are possible, but not desirable. The selectivity to ethane shows a similar

256 behavior for the catalyst with 5 wt% and 10 wt% iron loading, with a minimum of selectivity to
257 ethane at around 60 °C and higher selectivity to ethane at higher and lower temperatures. The
258 catalyst with 5 wt% iron loading shows the highest overall selectivity to ethane. It is noticeable,
259 that the selectivity of the catalyst with 1 wt% iron loading decreases with increasing temperature.
260 Therefore, the selectivity seems to be related to iron loading and particle size respectively,
261 indicating that low iron loadings lead to excellent selectivities of the catalyst. To evaluate the
262 activity of the catalysts per gram of active component, the reaction rate for the hydrogenation of
263 acetylene is determined.
264



265
266 *Figure 6: Reaction rate of the acetylene hydrogenation normalized by the mass of iron..*

267
268 The calculation of the reaction rates show that the catalyst with 1 wt% iron loading has the highest
269 overall values, followed by the catalysts with 5 wt% and 10 wt% iron loading. While the catalysts
270 with 5 wt% and 10 wt% iron loading show an approximate linear increase of the reaction rate, the

271 catalyst with 1 wt% iron loading shows an approximate exponential progression. Therefore, the
272 catalyst with an iron loading of 1 wt% exceeds the reaction rates of catalysts with 5 wt% and
273 10 wt% iron loading. The results underline the high catalytic activity of iron catalysts with lower
274 iron loading.

275 The results of the catalytic tests of iron-based catalysts with iron loadings of 1 wt%, 5 wt% and
276 10 wt% show excellent activity and selectivity in the acetylene hydrogenation under industrial
277 front-end conditions, especially for the catalyst with the lowest iron loading. Furthermore, the
278 catalytic activity exceeds that of unsupported iron nanoparticles, clearly demonstrating the
279 improved properties of the supported catalysts.

280 **4 Conclusion**

281 The goal of this work was to improve the catalysts' properties and the catalytic activity of
282 monometallic iron catalysts by supporting on alpha alumina and to underline the great suitability
283 of iron as catalyst in industrial relevant applications. In this work, catalysts with iron loadings of
284 1 wt%, 5 wt% and 10 wt% were synthesized by incipient wetness impregnation using water and
285 acetone as solvents. The catalysts were calcined, reduced and tested in the selective acetylene
286 hydrogenation under industrial front-end conditions. An activation behaviour of the catalysts due
287 to the contact of the catalysts with air after the reduction is observed. After reaching a plateau in
288 activity at 90 °C, the supported iron nanoparticles show excellent acetylene conversion of as well
289 as excellent selectivities towards ethylene. No significant ethylene conversion was observed. This
290 work demonstrates the great suitability of supported iron nanoparticles, especially for low iron
291 loadings. The results show the need for further research in the development of iron-based catalysts.
292 To increase the catalytic activity and enhance the reproducibility of the reduction process, the

293 development of a reactor concept with in situ reduction is important. This will shorten the
294 activation phase and might lead to increased catalytic activity. Furthermore, the resilience of iron
295 based catalysts against carbon monoxide in the reaction mixture must be tested and the effect on
296 the activity and selectivity needs to be monitored. This is important to evaluate the suitability as
297 industrial relevant catalyst. The development of iron-based bimetallic catalyst systems is of interest
298 for the optimization of the catalytic activity and selectivity. Lastly, testing of different shaped
299 α -alumina supports for improved flow behaviour should be part of further research and catalyst
300 development.

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304

305 **Conflict of Interests**

306 The authors declare no conflict of interest.

307

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