

Understanding the impact of silicon compounds on metallic catalysts through experiments and multi-technical analysis

Anne-Claire Dubreuil, Fabien Chainet, Rui Miguel De Sousa Bartolomeu, Filipe Manuel Marques Mota, Josselin Janvier, Charles-Philippe Lienemann

► To cite this version:

Anne-Claire Dubreuil, Fabien Chainet, Rui Miguel De Sousa Bartolomeu, Filipe Manuel Marques Mota, Josselin Janvier, et al.. Understanding the impact of silicon compounds on metallic catalysts through experiments and multi-technical analysis. *Comptes Rendus Chimie*, Elsevier Masson, 2017, 20 (1), pp.55 - 66. <10.1016/j.crci.2016.05.020>. <hal-01566173>

HAL Id: hal-01566173

<https://hal-ifp.archives-ouvertes.fr/hal-01566173>

Submitted on 20 Jul 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Understanding the impact of silicon compounds on metallic catalysts through experiments**
2 **and multi technical analysis**

3
4 **Compréhension de l'impact de composés silicés sur des catalyseurs métalliques par une**
5 **méthodologie couplant expérimentation et analyses multi-techniques**

6
7 A-C. Dubreuil*, F. Chainet, R. Bartolomeu, F. Marques Mota, J. Janvier, C-P. Lienemann

8
9 *Corresponding author. Phone: +33 4 37 70 28 29

10 E-mail: anne-claire.dubreuil@ifpen.fr

11 IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

12
13 **Abstract:**

14 The presence of silicon in petroleum products is a major issue due to its poisoning effect on
15 catalysts. The aim of this work is to combine silicon speciation and poisoning tests. Cyclic
16 siloxanes were the main silicon species found in petroleum products. Other silicon compounds,
17 comprising reactive groups (hydroxy, methoxy and hydroperoxy), were also recovered but at
18 trace levels using GC-ICP/MS. Five well-chosen silicon compounds were used to poison
19 Pd/alumina catalysts. Only dimethoxydimethylsilane poisons Pd-catalysts while
20 polydimethylsiloxane (PDMS) has no effect on their activities in buta-1,3-diene hydrogenation.
21 Unexpectedly, triethylsilane, triethylsilanol and even octamethylcyclotetrasiloxane (D₄) exhibit a
22 promoting effect. An interpretation of the phenomena based on various characterizations is
23 proposed.

24
25 **Keywords:**

26 Silicon, Pd catalyst, poison, promoter, buta-1,3-diene hydrogenation, speciation,
27 octamethylcyclotetrasiloxane

28

29

30

31

32

33 **Résumé :**

34 La présence du silicium dans les produits pétroliers est un problème majeur en raison de son effet
35 poison sur les catalyseurs. Le but de ce travail est de réaliser une spéciation du silicium et des
36 tests d'empoisonnement associés. Les siloxanes cycliques sont les composés majoritaires
37 retrouvés dans les produits pétroliers. D'autres molécules silicées, comprenant des groupements
38 réactifs (hydroxy, méthoxy and hydropéroxy) ont également été caractérisées, par GC-ICP/MS,
39 mais à l'état de traces. L'impact du silicium sur l'activité en hydrogénation du buta-1,3-diene de
40 catalyseurs Pd supportés sur alumine a été étudié au moyen de cinq espèces silicées choisies en
41 accord avec les résultats de la spéciation. Seul le diméthoxydiméthylsilane a un effet poison. Le
42 polydiméthylsiloxane (PDMS) ne montre aucun effet. De façon inattendue, le triéthylsilane, le
43 triéthylsilanol et également l'octaméthylcyclotétrasiloxane (D₄) montrent au contraire un effet
44 promoteur. Une interprétation des phénomènes est proposée sur la base de différentes
45 caractérisations.

46

47

48 **Mots-clés :**

49 Silicium, Catalyseur Pd, poison, promoteur, hydrogénation du buta-1,3-diène, spéciation,
50 octaméthylcyclotétrasiloxane

51

52

53

54	1	INTRODUC TION	4
55	2	MATERIALS AND METHODS	7
56	2.1	CATALYSTS PREPARATION.....	7
57	2.2	APPARATUS FOR POISONING AND CATALYTIC TESTS.....	7
58	2.3	POISONING PROCEDURE WITH SILICON COMPOUNDS.....	7
59	2.4	CATALYTIC TEST.....	8
60	2.5	SAMPLES.....	9
61	2.6	ANALYTICAL TECHNIQUES.....	10
62	2.6.1	Catalysts characterization.....	10
63	2.6.2	Liquid effluent characterization.....	11
64	3	RESULTS AND DISCUSSION	11
65	3.1	IDENTIFICATION OF REAL SILICON SPECIES.....	11
66	3.2	RESIDUAL ACTIVITY IN BUTA-1,3-DIENE HYDROGENATION OF SI-MODIFIED CATALYSTS.....	14
67	3.3	CHARACTERIZATION OF SI-MODIFIED CATALYSTS.....	15
68	3.3.1	Si content on Si-modified catalysts.....	15
69	3.3.2	Silicon deposition.....	16
70	3.3.3	Pd surface area of Si-modified catalysts.....	18
71	4	CONCLUSIONS	19
72		ACKNOWLEDGMENTS	20
73		TABLES AND FIGURES	21
74		REFERENC ES	22

75

76

1 Introduction

Silicon is known to be a severe poison for catalysts used in refining and petrochemical processes [1–6]. The deactivation of the catalyst leads to its untimely replacement and induces a great economic loss in the oil and gas industry [3][7]. However, contrary to other poisons, upstream silicon traps are scarcely used for technical and economic reasons.

It is widely assumed that the presence of silicon in petroleum products originates from the use of polydimethylsiloxanes (PDMS) as antifoaming additive to avoid emulsion phenomenon in different processes such as oil recovery, distillation, coking, visbreaking [8,9]. However, despite its rather good thermal stability (up to 300°C), PDMS degrades during thermal cracking of hydrocarbons, which is generally operated at 500°C or above [10]. Several authors [10–14] have studied the thermal degradation of PDMS under inert gas and air. Cyclic siloxanes (D_n) were identified as the major degradation products of PDMS with some trace of linear polysiloxanes [12]. Moreover, α,ω -dihydroxy polydimethylsiloxanes, which are known to be reactive silicon compounds, can be formed under environmental conditions of degradation by PDMS hydrolysis [15,16]. However, no study was reported under process refining conditions to evaluate the possible recombination between PDMS degradation products and carbon radicals. Moreover, the representativity of the analysed petroleum product samples appears as a major issue since these reactive silicon species could evolve between the on-site sampling and the analysis in the laboratory. This step could change the nature of the silicon species and alter the identification of the silicon species responsible of the catalyst poisoning.

Literature review on poisoning reported that silicon species can have a very different effect on catalyst depending on the composition of the catalyst [17,18], on the experimental conditions and especially on the chemical nature of the silicon molecule [19–21]. This means that, without knowing the chemical structure of silicon species present in petroleum products, it is impossible to study silicon effect on catalysts.

In petroleum products, only total silicon concentration is usually measured by inductively coupled plasma optic emission spectroscopy (ICP-OES) [22] or by inductively coupled plasma mass spectrometry (ICP/MS) [23] but no information about the chemical structure is given. Trace level concentrations, ranging from several hundred $\mu\text{g}/\text{kg}$ to several mg/kg in petroleum products [24], increase the difficulty for the identification of silicon species. To sum up, possible evolution

107 of species, trace level concentrations and complexity of gasoline sample, containing around 200
108 components [24], induce a real analytical challenge to achieve silicon speciation.
109 More recently, Chainet *et al.* [25–27] have proposed a methodology combining the production of
110 fresh PDMS degradation products at high silicon concentration under refining conditions using a
111 pilot plant and the development and application of a multi technical strategy to characterize
112 silicon species. Different powerful analytical tools (GC/MS in single ion monitoring (SIM) mode
113 [24], Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) [28], heart-
114 cutting gas chromatography coupled to time of flight mass spectrometry (GC-GC/TOFMS) [29]
115 and GC-ICP/MS [30]) were developed using model molecules in solvent and spiked gasolines.
116 PDMS degradation samples were obtained by heating PDMS at 500°C in a mixture of n-
117 heptane/xylene at different residence times and in the presence of steam or not [25]. The
118 innovative analytical strategy was then directly applied to PDMS degradation samples to avoid
119 possible evolution and to be sure that silicon species present when sampling stay in their native
120 form. This global analytical approach is here applied to gasoline samples, containing very low
121 amount of total silicon, in order to identify the real silicon species present in these feedstocks and
122 potentially identify the ones responsible of downstream catalysts poisoning.
123 Modification of alumina or of metallic catalysts by silicon species is widely reported in literature.
124 Various silicon compounds, such as PDMS, tetraorthosilicate (TEOS), siloxane, silanol, are used
125 to modify the acidic-basic properties of alumina [31,32] or to improve its hydrothermal resistance
126 [33]. Authors agree on a grafting mechanism of these silicon compounds on the alumina surface,
127 converting surface hydroxyl groups to generally hydrophobic Si-containing groups. Siloxane
128 compounds and disilazane compounds are also known to improve the catalytic performance of
129 hydrogenation catalysts [34,35] or hydrotreatment catalysts [36]. Either activity is promoted or
130 deactivation resistance is increased. Some poisoning effects are also reported with these silicon
131 compounds. For instance, silylation with disilazane ((Me₃Si)₂NH) at 100°C on oxygen or hydrogen
132 stream on Pt-based catalysts results on a decrease in activity for hydrogenation of alkenes or
133 alkynes [37]. Also, contacting Pt-based catalysts with hexamethyldisiloxane (L₂) at 350°C in air
134 results on a decrease in activity for oxidation of volatile organic compounds [38–40]. Several
135 studies also review relationships between catalyst properties and its propensity to be poisoned by
136 silicon species [19,41–47]. So, a decrease in the number of metallic sites available for reaction
137 and consequently a decrease in hydrogenation activity of alkenes, benzene or dienes have been

138 reported for metallic catalysts (Pd, Ni, Pt) supported on silica or on alumina after being contacted
139 with silane compounds, such as silane (SiH_4), triethylsilane (Et_3SiH), tetraethylsilane (Et_4Si) or
140 hexamethyldisilane (Me_6Si_2), under H_2 flow or inert flow and at high temperature (250°C).
141 Authors agree on strong interactions between silicon species and catalyst but the nature of
142 metallic surface modification is not yet clearly identified. Either geometric effect due to surface
143 reconstruction [44] or thin overlayers of silicon residues [4] or silicates (Si_xO_y) covering and
144 blocking the surface sites [38–40] or electronic effect [19,47] have been suggested. Smith *et al.*
145 [42] also studied reactivation of such poisoned catalysts by oxidation and reduction treatment.
146 This reactivation is structure sensitive and catalysts with smaller metal crystallites can achieve an
147 hydrogenation activity greater than the original one.

148 However, as far as we know, no poisoning study was achieved yet with silicon compounds
149 derivated from PDMS degradation, especially cyclic siloxanes (D_n) which are the main
150 degradation products, nor in hydrogenation processes operating conditions. This was hampered
151 on the one hand by the absence of knowledge on silicon speciation in the oil and gas industry,
152 and on the other hand by the low amount of silicon in feedstocks and by the presence of other
153 contaminants (sulfur for example) that could hide the real effect of silicon.

154 In this work, we compare the silicon speciation obtained in PDMS degradation samples and in
155 real gasolines using our analytical strategy to select several representative silicon species with
156 various chemical functions. Then, their effect on Pd-based catalysts for selective hydrogenation
157 of gasoline is studied. Poisoning conditions (under H_2 pressure, temperature, no exposure of the
158 catalyst to air between poisoning and catalytic test, ...) were chosen to be as representative as
159 possible for poisoning in industrial units. However, silicon content in the poisoning solution is
160 much larger than in real gasolines, in order to reduce poisoning time and to reach significant
161 silicon content in the catalyst. Hydrogenation of buta-1,3-diene, chosen as model reaction, was
162 run in a semi-batch stirred reactor, in the liquid phase under 10 bar of H_2 . Further
163 characterizations were achieved on Si-modified catalysts to discuss the effect of various silicon
164 compounds.

165

166 2 **Materials and methods**

167 2.1 *Catalysts preparation*

168 Two Pd-based catalysts were prepared by incipient wetness impregnation, using palladium nitrate
169 as precursor and δ -alumina as support. Two aluminas with different specific surface areas $S_{\text{BET}} =$
170 $60 \text{ m}^2/\text{g}$ (alumina A') and $S_{\text{BET}} = 130 \text{ m}^2/\text{g}$ (alumina B') were used. After impregnation, the
171 solids were dried overnight at 120°C and calcined under air flow at 480°C during 2 hours. Both
172 catalysts A and B, prepared respectively on the alumina A' and B', present a Pd loading of 0.3
173 wt. %, determined by ICP-OES. Prior to poisoning and testing, catalyst beads were crushed and
174 sieved in the range $200 - 355 \mu\text{m}$. A quantity of 1 g of catalyst was treated under H_2 flow at
175 150°C for 2 hours (flow rate = 1 NL/h, temperature rate = $300^\circ\text{C}/\text{h}$) and once cooled to room
176 temperature was transferred into the reactor without any contact with air.

177 2.2 *Apparatus for poisoning and catalytic tests*

178 Poisoning and hydrogenation tests were carried out successively in the same apparatus, a
179 stainless steel semi-batch stirred reactor, in liquid phase under 10 bar of H_2 . Both poisoning
180 conditions and absence of air exposure between poisoning step and catalytic test were chosen so
181 as to be representative for poisoning in industrial units.

182 The total volume of the reactor is 250 mL. The reactor is equipped with a gas inducing turbine
183 impeller, baffles, a thermowell, a pressure transducer, a gas inlet port and a liquid sample port.
184 The pressure in the reactor is maintained constant by a pressure regulator connected to a
185 hydrogen storage vessel.

186 2.3 *Poisoning procedure with silicon compounds*

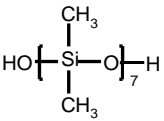
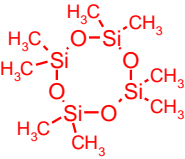
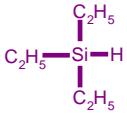
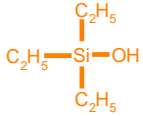
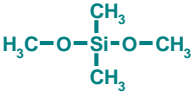
187 The reduced Pd-based catalyst is contacted with a mixture of one silicon compound in n-heptane
188 (140 mL of previously degassed n-heptane), without any contact with air. Then the reactor is
189 sealed, purged and pressurized under 10 bar of H_2 , and heated to 50°C . This temperature is
190 maintained for 5 hours, with high stirring velocity (1600 rpm).

191
192 Several kinds of silicon compounds, presented in Table 1, were considered. The choice of these
193 molecules is discussed in paragraph 3.1. Si content in n-heptane was ranged between 1 wt. % and

194 3 wt. %. As often in laboratory poisoning tests, higher poison concentration and shorter exposure
 195 time than in industrial units are used [39]. Poisoning procedure was also performed on
 196 uncrushed Pd catalysts: after reduction, and without any contact with air, catalyst beads are put
 197 into a toric basket fitted to the reactor. Samples are named in the following way: X-Y-Z, with X
 198 being the catalyst or alumina reference (A, B, A', B'), Y the silicon compound (TESiOH, D₄,
 199 DMDSi, PDMS, TESI) and Z the Si content in the poisoning solution (in wt. %). For example,
 200 sample A-D₄-1 means catalyst A contacted with a 1 wt. % Si solution of D₄ in n-heptane.

201 **Table 1**

202 Physical properties of model silicon compounds considered in this work.

Compound	Dihydroxy tetradecamethylsiloxane (PDMS)	Octamethyl cyclotetrasiloxane (D ₄)	Triethylsilane (TESi)	Triethylsilanol (TESiOH)	Dimethoxy dimethylsilane (DMDSi)
Chemical structure					
Supplier	Sigma-Aldrich, Saint-Quentin-Fallavier, France				
Molecular weight (g/mol)	550	297	116	132	120
Silicon/Molecule (wt. %)	35.7	37.9	24.2	21.2	23.4
Boiling Point (°C)	182	175	107-108	86-87	81.4

203

204 2.4 Catalytic test

205 Once the poisoning procedure is completed, the reactor is cooled down to 17°C and about 7 g of
 206 buta-1,3-diene are introduced in the liquid phase. Hydrogenation of buta-1,3-diene is run under
 207 10 bar of H₂, at 17°C and with a high stirring velocity (1600 rpm). Experimental conditions have
 208 been previously optimized to avoid mass transfer limitations. The H₂ consumption can be
 209 measured accurately by recording the pressure drop inside the hydrogen storage vessel. The
 210 reacting mixture is also sampled over time and analyzed by gas chromatography coupled to flame
 211 ionization detector (GC-FID). Note that silicon compounds were still present in the reactor during
 212 the hydrogenation test but they should not poison the catalyst since the temperature is low and the
 213 contact time is very short (tens of minutes) compared to poisoning procedure. Moreover, it was
 214 verified that there is no effect due to the operating conditions of the poisoning procedure on a
 215 fresh Pd-catalyst contacted with n-heptane only (with no silicon content).

216 Typical evolution of the H₂ consumption versus time and typical variations of buta-1,3-diene and
217 reaction products concentrations versus time are reported in Fig. 1. Buta-1,3-diene is
218 hydrogenated into butenes (but-1-ene and *cis* and *trans* but-2-enes) and hydrogenation of butenes
219 into butane only occurs as buta-1,3-diene is completely consumed, as reported in literature for
220 Pd-based catalyst [48]. Therefore, rate constants were based on the rates of consumption of H₂ for
221 the hydrogenation of buta-1,3-diene into butenes (r_1) and for the hydrogenation of butenes into
222 butane (r_2). Catalyst activity is defined as r_1 and butenes selectivity is expressed as the ratio of the
223 consecutive hydrogenation steps (r_1/r_2). Residual activity of the Si-modified catalyst with respect
224 to fresh catalyst is determined according to the following equation:

225

$$226 \text{ Residual activity (\%)} = 100 \times r_1(\text{Si-modified catalyst}) / r_1(\text{fresh catalyst}) \quad (\text{Equation 1})$$

227 **2.5 Samples**

228 To determine real silicon species potentially responsible for catalyst poisoning, two types of
229 samples were analysed using a multi technical strategy: real gasolines with low content of silicon
230 and PDMS degradation samples with high silicon content.

231 Naphtha and pyrolysis gasoline samples, coming from different thermal cracking processes
232 (coking, steam cracking) of various refineries, have been previously analysed using our multi
233 technical strategy [24,28–30]. All samples characteristics are detailed in Table 2. Silicon contents
234 in naphtha and gasoline are very low, which makes silicon speciation so difficult. From these
235 samples, naphtha 2 which comes from a steam cracking process was selected to illustrate our
236 approach.

237 One of the PDMS degradation samples previously produced using the IFPEN pilot plant was also
238 chosen (test B) for this study [25]. It was obtained at 500°C and with a short residence time of 0.5
239 s and in the presence of 50% of steam to simulate steam cracking process conditions. All
240 operating conditions were previously summarized in Chainet *et al.* [25]. All samples were stored
241 at -10°C to minimize the possible evolution of silicon species and were characterized using a
242 multi technical approach, already detailed in Chainet *et al.* [25–27]. The Si concentration was
243 higher in PDMS degradation sample than in real samples to obtain a better identification of
244 silicon compounds (Table 2).

245 **Table 2**

246 Total silicon concentration of samples measured by X-Ray Fluorescence (XRF) or ICP-OES.

Samples	Type	Si (mg of Si/kg)	
		XRF	ICP-OES
Naphtha 1	Steam cracking feed	<LOQ	0.528
Naphtha 2	Steam cracking feed	<LOQ	0.556
Pyrolysis gasoline 3	Steam cracking product	<LOQ	1.02
Pyrolysis gasoline 5	Steam cracking product	<LOQ	2.53
Naphtha 4	Coker	<LOQ	1.5
Test B (IFPEN)	PDMS degradation sample	2482 ± 155	nd

247 nd: not determined

248

249 **2.6 Analytical techniques**250 **2.6.1 Catalysts characterization**

251 Further characterizations were made on catalysts once poisoning procedure and/or catalytic test
 252 were completed. Catalyst is washed several times with n-heptane and dried at 35°C before
 253 analysis.

254 Si content on the catalyst was measured using an Axios X-ray fluorescence spectrometer (XRF)
 255 (PANalytical, Almelo, the Netherlands) operating at 125 mA and 32 kV and equipped with an
 256 automatic sample changer. Catalyst was grinded finely to homogenize the sample and mixed with
 257 Spectroflux. The powder mixture was heated in a platinum crucible at 1000°C to obtain a
 258 homogeneous bead. The bead was then exposed to primary X-rays and the characteristic X
 259 radiations of silicon are measured to determine the silicon content with a calibration curve.

260 Infrared spectra of the carbonaceous species present in the samples were recorded by
 261 transmission on a Bruker vertex 70 spectrometer (64 scans). Prior to IR analysis, self-supported
 262 wafer of the sample (*ca.* 20 mg) is placed in a quartz IR cell and activated in situ at 50°C
 263 overnight under secondary vacuum (10^{-6} mbar).

264 The radial profiles of Pd, Al and Si concentrations along the diameter of the catalyst beads were
 265 obtained by Electron Probe Microanalysis (EPMA). The beads were placed in a plastic mould
 266 and embedded with a viscous epoxy resin (pre-polymerized in oven at 70°C during 20 minutes).
 267 After hardening, the samples were polished in order to obtain a cross section of the beads. The
 268 preparations were then coated by a 20 nm thick carbon layer. The measurements were performed
 269 with a JEOL JXA 8100 or a Cameca SX100 microprobe, both equipped with five wavelength-
 270 dispersive spectrometers. The electron beams conditions were 20 kV acceleration voltage, 200

271 nA probe current and a focused beam. Pd was measured using the $L\alpha$ -line on a pentaerythritol
272 (PET) crystal, Al and Si using the $K\alpha$ -line on a thallium acid phthalate (TLAP) crystal. The
273 counting times are 40 s on the peaks and 10 s on the backgrounds (measured on each side of the
274 peak). Pure Pd, alumina and silica are used as standards. Such radial profiles were acquired in
275 five different beads.

276

277 2.6.2 *Liquid effluent characterization*

278 The multi technical approach used for silicon speciation was previously presented in details for
279 the analysis of the liquid effluent [27]. A flow chart of this analytical strategy is illustrated in Fig.
280 2. All apparatus were already detailed in our previous works [24–27,29,30]. In this paper,
281 naphtha 2 and PDMS degradation were analyzed using GC/MS SIM and GC-ICP/MS (Fig. 2).
282 The GC/MS SIM method allows the quantification of known silicon compounds such as cyclic
283 siloxanes. For unknown compounds, *ie* not commercially available, GC-ICP/MS is required to
284 determine the retention time of all silicon compounds [30]. Based on the retention time of cyclic
285 siloxanes always present in all samples, retention indices were calculated and allowed a unique
286 value of retention for GC/TOFMS, GC/MS SIM and GC-ICP/MS [27,30]. According to our multi
287 technical approach based on MS techniques (GC/TOFMS, FT-ICR/MS and MSⁿ) (Fig. 2), a
288 chemical structure and a raw formula were assigned to each silicon compound detected by GC-
289 ICP/MS if its retention index was already known [30]. Thanks to this characterization, silicon
290 species could be identified both in PDMS degradation sample and in naphtha 2, in order to
291 validate our approach and to study the silicon effect on catalyst.

292

293 3 Results and discussion

294 3.1 *Identification of real silicon species*

295 Fig. 3 illustrates GC/MS SIM chromatograms obtained for naphtha 2 and PDMS degradation
296 sample. For the naphtha sample, an internal standard (M_4Q) was used for the quantification. This
297 work was previously published in Chainet *et al.* [24]. Cyclic siloxanes (D_n) are the major silicon
298 species identified both in PDMS degradation samples (about 95% of the total amount of silicon
299 species) and in gasolines (D_3 - D_5). These results confirmed that cyclic siloxanes (D_n) are the main

300 thermal degradation products of PDMS as previously reported in the literature [7,10,12,14]. For
301 the first time, the comparison of real gasoline and representative PDMS degradation sample
302 demonstrates that cyclic siloxanes are the main silicon species in petroleum products at trace
303 levels compared to PDMS degradation samples.

304
305 Chainet *et al.* [26,27] have previously demonstrated that other silicon species (about 5% of the
306 total amount of silicon species), almost never characterized before and present at trace levels
307 compared to cyclic siloxanes were also present in all petroleum cuts, from the gas fractions to
308 heavy cuts. More than 100 silicon species from 12 chemical families were characterized and
309 possessed reactive functions (hydroxy, methoxy or hydroperoxy) able to react very rapidly with
310 the catalyst and potentially cause its deactivation. Scales-up of the GC-ICP/MS chromatograms
311 of the D₅ elution zone for PDMS degradation sample (a) and naphtha 2 (b) are presented for
312 example in Fig. 4. Using retention indices and MS results for silicon species [27,30], the same
313 three molecules were characterized both in PDMS degradation sample and in naphtha 2.

314 According to previous works [28,30,49], a synthesis of the different silicon species characterized
315 only in gasoline fractions (35°C<boiling points<200°C) are detailed in Table 3 and are presented
316 with their number of silicon atoms and identified chemical structure. The three silicon
317 compounds (Fig. 4) characterized both in PDMS degradation sample and in naphtha (Table 3) are
318 also detailed. Except for silanes and α,ω -dihydroxy polydimethylsiloxanes, all silicon species,
319 with various numbers of silicon atoms, were characterized both in PDMS degradation samples
320 and in real gasoline samples using our multi technical strategy [28,30,49]. These results fully
321 confirmed our approach because same silicon species were recovered between real samples and
322 PDMS degradation samples. Moreover, even if the concentrations of these species in naphtha are
323 obviously very low compared to cyclic siloxanes, we were able to detect and identify them, even
324 in low concentrated real naphthas. Despite their trace level concentrations, these species could
325 have an effect on catalyst considering their reactive functions. In the first part of this work, the
326 representative speciation of silicon allowed us to select the real silicon species formed during
327 refining processes. In the second part, their impact on downstream catalysts will be studied. From
328 all the identified silicon species, five compounds were chosen. These molecules and their
329 characteristics were already presented in Table 1. The selection was made so as to take into
330 account all different chemical forms (cyclic and linear) and possible reactive functions (Si-OH,

331 Si-H, Si-OCH₃). Practical considerations were also taken into account: commercial availability,
 332 ease of use (in liquid phase at ambient temperature) and with a boiling point in the gasoline range
 333 (35-200°C).

334

335 **Table 3**

336 Silicon compounds characterized in both PDMS degradation samples and in real gasoline samples.

Molecules	Chemical Structure	Refs.	Molecules	Chemical Structure	Refs.
α,ω -dihydroxy polydimethylsiloxanes		nc	Heptamethylhydroxycyclo tetrasiloxane (Si ₄)		[49]
Cyclic siloxanes (D ₃ -D ₅)		[24,27-30]	Methyl(methylhydroperoxy) cyclic siloxane (Si ₄ -Si ₅)		[49]
Trimethylsilane Tetramethylsilane		nc	Di(ethoxy methyl) tetramethyl cyclo tetrasiloxane * (Si ₄)		[49]
Trimethylsilanol (Si ₁)		nc	Ethoxy nonamethyl cyclopentasiloxane (Si ₅)		[49]
Dimethoxy tetramethylsilane (Si ₂)		[28]	1,3,3,5,5,7-hexamethyl-2,4,6,8,9-pentaoxa-1,3,5,7-tetrasilabicyclo[5.1.1]nonane (Si ₅)		[49]
Linear polydimethylsiloxanes (L ₂ -L ₅)		[24,29]	1,3,3,5,5,7,9,9-octamethyl-2,4,6,8,10-pentaoxa-1,3,5,7,9-pentasilabicyclo[5.3.1]undecane (Si ₅ -Si ₆)		[49]

337 n is the number of silicon atoms (Si_n)

338 nc: not characterized in real sample

339 * For this structure : a-R=EtO=R'=EtO or b-R=MeO and R'=PrO; Et: ethyl, Me: methyl, Pr: propyl

340

341

3.2 Residual activity in buta-1,3-diene hydrogenation of Si-modified catalysts

The comparison of catalytic performances in buta-1,3-diene hydrogenation between the different Si-modified samples is presented in Fig. 5 and in Table 4. Catalytic activities are expressed as “residual activities” compared to the activity of the fresh catalyst (which has not been contacted with any silicon molecule). Depending on the silicon compound, Si-modified samples exhibit either a lower activity than fresh catalyst, or a similar, or even a higher one. From the five silicon compounds used, only DMDSi poisons Pd-catalyst (“residual activity” lower than 100 %), while PDMS has no effect on catalytic activity and a promoting effect (“residual activity” higher than 100 %) is obtained with D₄, TESi and TESiOH. Even if some silicon species are known to enhance catalytic performances as described in the Introduction, these results are rather unexpected. Several authors [19,43–45] have shown a poisoning effect with silane compounds on Pd-based catalysts for diene or alkene or alkyne hydrogenation; however, poisoning procedure and silicon compound were different from the ones in this study. Moreover, authors [10–14] agree that cyclic siloxanes (D_n) are the main products of PDMS degradation and consequently these compounds are expected to be the one responsible for catalyst poisoning [2,6]. Moreover, this study is the first one about poisoning with D₄ in particular and it concludes to a promoting effect.

Both promoting effect with D₄ and poisoning effect with DMDSi are observed on the two Pd-based catalysts A and B (Fig. 5 and Table 4). These effects are enhanced on catalyst B which is supported on the alumina with the highest specific surface.

Butenes selectivities are also reported in Table 4. Effect on butenes selectivity depends on the silicon compound. Butenes selectivity is not modified significantly with DMDSi; for fresh Pd-catalyst as well as for DMDSi-modified catalyst, r_1/r_2 is about 3, which means that hydrogenation of butenes into butane is about 3 times slower than hydrogenation of buta-1,3-diene into butenes. But, butenes selectivity is slightly enhanced with PDMS, D₄ and TESiOH; hydrogenation of butenes is then about 6 times slower than hydrogenation of buta-1,3-diene. Moreover, a large butenes selectivity enhancement is obtained with TESi, hydrogenation of butenes being about 15 times slower than hydrogenation of buta-1,3-diene. Whereas butenes selectivity degradation seems to be linked with the loss of activity (with DMDSi), selectivity enhancement is linked with the not-modified activity (with PDMS) or promoted activity (with D₄, TESiOH, TESi cases). Such relations between activities and selectivities are reported in literature on bimetallic catalysts

373 for hydrogenation of alkyne or hydrogenation of dienes [50], even if most of the observations
 374 report an activity decrease and a selectivity enhancement [51]. For example, Si-modified Pd
 375 catalysts prepared by chemical vapor deposition of triethylsilane exhibit an improved selectivity
 376 in alkyne hydrogenation for a given activity [19,44].

377
 378 **Table 4**
 379 Catalytic performances in buta-1,3-diene hydrogenation for Si-modified Pd-based catalysts expressed as
 380 residual catalytic activities reported to fresh catalyst and as butenes selectivity. Si contents in the samples
 381 are also reported.

Sample (**)	Si content in the catalyst (wt. ppm)	Residual activity ($r_1/r_{1_fresh\ catalyst}$) (%)	Butenes selectivity (r_1/r_2) (%)
A	0	100	3.5 ± 1.1
A-PDMS-1	nd	99 ± 11	6.9 ± 2.5
A-D ₄ -1	nd	146 ± 17	5.0 ± 1.2
A-TESi-1	nd	123 ± 14	14.3 ± 6.3
A-TESi-3	7758 ± 160	222 ± 31	15.4 ± 7.0
A-TESiOH-1	nd	124 ± 14	5.7 ± 1.3
A-TESiOH-3	1283 ± 70	186 ± 26	5.8 ± 1.3
A-DMDSi-1	5288 ± 130	77 ± 8	4.0 ± 1.0
A-DMDSi-3	5439 ± 130	52 ± 7	2.7 ± 1.5
B-D ₄ -1 (*)	11000 ± 220	248 ± 5	nd
B-DMDSi-1	10942 ± 220	37 ± 6	nd

382 nd : not determined

383 (*) poisoning procedure at 70°C

384 (**) Samples are named in the following way: X-Y-Z, with X being the catalyst or alumina reference (A,
 385 B, A', B'), Y the silicon compound (TESiOH, D₄, DMDSi, PDMS, TESi) and Z the Si content in the
 386 poisoning solution (in wt. %). For example, sample A-D₄-1 means catalyst A contacted with a 1 wt. % Si
 387 solution of D₄ in n-heptane.

388 3.3 Characterization of Si-modified catalysts

389 Further characterizations were made on Si-modified catalysts or Si-modified aluminas in an
 390 attempt to explain the poisoning effect and promoting effect described above.

391 3.3.1 Si content on Si-modified catalysts

392 Si contents in the Si-modified catalysts are reported in Table 4. Si content in the catalyst depends
 393 on the silicon compound. For a given catalyst and a given Si content in the poisoning solution, Si
 394 content in the catalyst increases with the following order: TESiOH < DMDSi \cong D₄ < TESi. Thus,
 395 the presence of a Si-H bond in the silicon compound increases Si deposition in the catalyst. This
 396 is in agreement with Molnar *et al.* [21] who correlated the increasing quantity of Si retained on
 397 Cu- or Rh- or Pt-supported catalysts and the increasing number of Si-H bonds in the silicon

398 compound (or the decreasing number of Si-C bonds). No relation is observed between Si content
 399 in the catalyst and poisoning or promoting effect: for instance, on catalyst B, with Si content of
 400 about 11000 wt. ppm, promoting effect is observed with D₄ and poisoning effect with DMDSi. It
 401 should be noted that the effect (promoting or poisoning effect) is increasing with the Si content.

402 3.3.2 Silicon deposition

403 Infrared spectra of the carbonaceous species present in the Si-modified catalysts are shown in
 404 Fig. 6. Peaks assignment is given in Table 5. Typical C-H stretchings and bendings of the CH₃
 405 and CH₂ groups are clearly visible in TESI-modified catalyst and typical C-H stretchings of the
 406 CH₃ are clearly visible in DMDSi-modified catalyst, whereas, as expected, none of these peaks
 407 are present on fresh catalyst IR spectrum. Thus, silicon molecules are not decomposed during Si-
 408 poisoning procedure, but they are rather grafted on the catalyst, either on alumina surface and/or
 409 on Pd particles.

411 **Table 5**

412 Assignment of vibration bands in IR spectra showed in Fig. 6 [52]

Wavenumber (cm ⁻¹)	Assignment	Concerned sample
2964 - 2958	νCH_3 (asym)	A-TESI-1 and A-DMDSi-1
2915	νCH_2 (asym)	A-TESI-1 only
2904	νCH_3 (sym)	A-DMDSi-1 only
2881	νCH_2 (sym) and νCH_3 (sym)	A-TESI-1 only
1463	δCH_2 (sym) and δCH_3 (asym)	A-TESI-1 only
1417	δCH_3 (sym)	A-TESI-1 only
1260	Si-CH ₃	A-DMDSi-1 only
1239	Si-CH ₂ -CH ₃	A-TESI-1 only

413 νCH_n : stretching vibrations of alkyl group CH_n (n=2 or 3) - δCH_n : bending vibrations of alkyl group CH_n
 414 (n=2 or 3) - sym: symmetric - asym: asymmetric

416 Another evidence of silicon molecules grafted on catalyst is given by gas phase analysis at the
 417 end of the poisoning procedure with DMDSi. Some CH₄ was detected in the gas phase, which
 418 means Si deposition is made by hydrogenolysis. Such an evidence was obtained both with Si-
 419 modified alumina and Si-modified Pd catalyst.

420 Si location inside the support beads was analyzed by Electron Probe Microanalysis. For these
 421 characterizations, poisoning procedure was performed on uncrushed Pd catalysts and samples
 422 were analyzed immediately after the poisoning procedure was completed. As shown in Fig. 7, Si
 423 is located everywhere in the support beads, both in the inner core and in the outer shell containing

424 also Pd particles. In the case of D₄ and DMDSi, as Si repartition is homogeneous all along the
425 beads diameter, silicon molecules would appear to be mainly grafted on the alumina surface.
426 Indeed, Si-poisoning experiments run on bare aluminas show that a large amount of Si is grafted
427 on alumina (Table 6). However, Si content grafted on Pd-based catalyst is slightly higher than on
428 bare alumina, which suggests some kind of affinity between Si and Pd particles: additionally to
429 be grafted on alumina surface, silicon molecules can be grafted on Pd particles surface or grafted
430 on alumina surface with a higher density at the vicinity of Pd particles. This affinity between Si
431 and Pd particles is much more pronounced in the case of TESi, since Si content is larger in the
432 outer shell containing Pd particles than in the inner core (Fig. 7.b). Si deposition on Pd particles
433 surface is also indicated by the loss of Pd surface area recorded on Si-modified catalysts. Pd
434 surface area, measured by CO chemisorption experiments using a dynamic method, is only 25 –
435 35 % of the initial surface area of fresh catalyst, for both TESi-modified catalyst and DMDSi-
436 modified catalyst.

437 Grafting of silicon species on both alumina support and metallic particles is described also by
438 Rahmani *et al.* [39,40] while poisoning Pt-catalysts with hexamethyldisiloxane (L₂ according to
439 notations in Table 3) at 350°C in air. They also reported a promoting effect of platinum on
440 deposition of silicon species on the catalyst surface. Kellberg *et al.* [4] also characterized Si
441 deposits on aged naphtha hydrotreatment (HDT) catalysts by ²⁹Si NMR spectroscopy and
442 described various surface species of modified silica gel. Moreover, Smith *et al.* [19] reported
443 strongly tri-adsorbed alkyl Si species and even Pd-Si alloy (silicon gradually coats the surface of
444 Pd particles and diffuses into the bulk of the Pd particle) [18,43] after silation by chemical vapor
445 deposition of triethylsilane at 250°C into flowing hydrogen. Shin *et al.* [44–46] described a
446 modified Pd surface composed of Pd, Si and SiO₂ obtained after chemical vapor deposition of
447 silane and oxidation at ambient temperature. So, various mechanisms of silicon deposition on
448 metallic supported catalysts can occur depending on poisoning conditions (silicon compound,
449 contact in gas or liquid phase, temperature, reductive or oxidative atmosphere...) and catalysts
450 properties (metallic phase, nature of the support ...).

451

452

453 **Table 6**

454 Si content on Si-modified aluminas and Si-modified Pd-catalysts.

Sample	Si content in the catalyst (wt. ppm)
B'-D ₄ -1 (*)	8500 ± 180
B-D ₄ -1 (*)	11000 ± 220
B'-DMDSi-1	9977 ± 200
B-DMDSi-1	10942 ± 220

455 (*) poisoning procedure at 70°C

456 3.3.3 Pd surface area of Si-modified catalysts

457 As mentioned above, a loss of Pd surface area is recorded on Si-modified catalysts. This is
458 consistent with the decrease of activity obtained with DMDSi-modified catalyst (Table 4 and Fig.
459 7). Such a diminution of metallic surface area is also described by Smith *et al.* [42], Shin *et al.*
460 [44] and other authors [20,37,39,40]. On the contrary, for TESi- and even D₄- or TESiOH-
461 modified catalysts, an increase of activity is obtained despite the decrease of Pd surface area
462 (Table 4 and Fig. 7). A quite similar effect is reported by Rahmani *et al.* [40] since Pt-catalyst
463 poisoned with L₂ exhibits a high activity in ethyl acetate oxidation despite an important loss of Pt
464 surface area; different kinds of Pt sites accessible for CO adsorption and for oxidation of ethyl
465 acetate are also mentioned. In our study, the butenes selectivity enhancement also observed with
466 these silicon compounds suggests some modification on electronic and/or geometric properties of
467 Pd particles [50]. Indeed, changing the electronic density of Pd affects the relative adsorption
468 strength of reactants, intermediates and hydrogen and thus catalyst activity and selectivity
469 [53,54]. Alternatively, the presence of strongly adsorbed Si species and of organometallic
470 fragments may block a part of the Pd active surface, which could favor some specific sites, or
471 may modify hydrogen adsorption on Pd, and thus modify selectivity [5,44,55–57]. These effects
472 are more pronounced for TESi-modified catalyst which presents a higher affinity between Pd and
473 Si, a higher butenes selectivity enhancement and a higher activity. Thus, for a given poisoning
474 procedure, silicon compounds with various chemical forms and reactive functions may differ in
475 their interactions with catalysts, which leads to a more or less noticeable either poisoning effect
476 or promoting effect. This illustrates once more the importance of choosing adequate silicon
477 compounds for laboratory studies. The effects of both a mixture of various silicon compounds
478 and the operating conditions of the poisoning procedure could also be studied.

479

4 Conclusions

480
481 Silicon compounds, coming from PDMS thermal degradation, are known to affect refining and
482 petrochemical catalysts. This work reported for the first time the combining approach between
483 silicon speciation and the study of their impact on Pd-based hydrogenation catalysts in
484 representative conditions for poisoning in industrial units.

485 The production of PDMS degradation samples associated to their analysis by a multi technical
486 strategy, mainly based on chromatography and MS techniques, allowed the characterization of
487 more than 100 silicon species. To be sure that silicon species, potentially responsible for catalyst
488 poisoning are in their native form during the analysis in the laboratory, silicon species identified
489 in PDMS degradation samples and in real gasolines were compared. Cyclic siloxanes (D_n) were
490 the major PDMS degradation products (about 95% of the total amount of Si). They were also the
491 main silicon species recovered in petroleum products, especially D_3 and D_4 in the gasoline cut.
492 Other silicon compounds, consisted of reactive groups such as hydroxy, methoxy and
493 hydroperoxy, were also recovered at trace levels (about 5%), both in PDMS degradation samples
494 and in gasolines using GC-ICP/MS.

495 Si-modified Pd / alumina catalysts were prepared by contacting well-chosen silicon compounds
496 in liquid phase at moderate temperature and under H_2 pressure. Five silicon compounds were
497 chosen thanks to the previous speciation study, PDMS, octamethylcyclotetrasiloxane (D_4),
498 triethylsilane (TESi), triethylsilanol (TESiOH) and dimethoxydimethylsilane (DMDSi), taking
499 into account previously identified chemical forms and reactive functions. Only DMDSi poisoned
500 Pd-catalysts while PDMS has no effect on the activity of the Pd catalysts. As silicon is known to
501 act as a severe poison, we expected that cyclic siloxanes (D_4), as the major silicon species in
502 gasolines, poisoned the Pd catalyst. On the contrary, TESI-, TESI OH- and especially D_4 -modified
503 catalysts, showed a promoting effect on both activity in buta-1,3-diene hydrogenation and
504 butenes selectivity. These effects, either promoting or poisoning effects, are more pronounced as
505 Si content is higher. Silicon molecules are not decomposed during this Si-poisoning procedure,
506 but they are rather grafted on the catalyst, both on alumina surface and on Pd particles. Combined
507 decreased Pd surface area and enhancement of activity and selectivity suggest some modification
508 on electronic and/or geometric properties of Pd particles.

509 These results clearly showed the importance of the representative speciation of silicon in gasoline
510 in order to study the effect of real species in contact with the catalyst during refining or

511 petrochemical processes. However, despite the poisoning conditions chosen to be as
512 representative as possible for poisoning in industrial units, higher poison concentration and
513 shorter exposure time were used, and care should be taken when extrapolating the results to a real
514 application.

515 **Acknowledgments**

516 Authors would like to thanks M. Rivallan (IR analysis), S. Carbonneaux (XRF), A-S. Gay
517 (EMPA) of the IFPEN Physics and Analysis division (Solaize, France) for characterization
518 results, discussion and support for interpretations, as well as N. Caillol for her kind proofreading.
519 Special acknowledgements go to O-F-X. Donard (IPREM, Pau, France) for giving us the
520 opportunity to perform GC-ICP/MS analysis.

521

522

Tables and Figures

523 **Table 1** Physical properties of model silicon compounds considered in this work.

524 **Table 2** Total silicon concentration of samples measured by X-Ray Fluorescence (XRF) or ICP-OES.

525 **Table 3** Silicon compounds characterized in PDMS degradation samples and in real gasoline samples.

526 **Table 4** Catalytic performances in buta-1,3-diene hydrogenation for Si-modified Pd-based catalysts
527 expressed as residual catalytic activities reported to fresh catalyst and as butenes selectivity. Si contents in
528 the samples are also reported.

529 **Table 5** Assignment of vibration bands in IR spectra showed in Fig. 6 [52]

530 **Table 6** Si content on Si-modified aluminas and Si-modified Pd-catalysts.

531

532 **Fig. 1.** Hydrogenation of buta-1,3-diene at 17°C and under 10 bar of H₂ for fresh Pd-catalyst A. Evolution
533 of the H₂ consumption (large line, left axis) versus time, and evolution of the composition of the mixture
534 of buta-1,3-diene and reaction products (right axis) versus time.

535 **Fig. 2.** Flow chart of the analytical strategy for the effluent characterization (Adapted from [25]).

536 **Fig. 3.** GC/MS SIM chromatograms of a typical PDMS degradation sample (test B) and a real naphtha
537 (naphtha 2).

538 **Fig. 4.** Scales-up of the GC-ICP/MS chromatograms for PDMS degradation sample (a) and naphtha 2 (b)
539 illustrating the D₅ elution zone (1: 1,3,3,5,5,7-hexamethyl-2,4,6,8,9-pentaoxa-1,3,5,7-
540 tetrasilabicyclo[5.1.1] nonane (C₈H₂₅O₆Si₅); 2: Di(ethoxy methyl) tetramethyl cyclotetrasiloxane
541 (C₁₀H₂₉O₆Si₄); 3: Octamethylmethyl(methylhydroperoxy) cyclopentasiloxane (C₁₀H₃₁O₇Si₅).

542 **Fig. 5.** Residual catalytic activities in buta-1,3-diene hydrogenation for Si-modified Pd-based catalysts.

543 **Fig. 6.** Scale-up of IR spectra in the 4000 – 2500 cm⁻¹ region (a) and in the 1800 – 1100 cm⁻¹ region (b),
544 for fresh catalyst A and catalyst A modified with DMDSi (sample A-DMDSi-1) and TESi (sample A-
545 TESi-1).

546 **Fig. 7.** Metallic repartition profiles for Al, Pd and Si versus support depth (measured by electron probe
547 microanalysis) for catalyst A modified with DMDSi (sample A-DMDSi-1) (a) and TESi (sample A-
548 TESi-1) (b), and catalyst B modified with D₄ (sample B-D₄-1) (c).

549

550

551

References

- 552 [1] P. Dufresne, *Appl.Catal.*, A 322 (2007) 67.
- 553 [2] M. Serban, M.P. Lapinski, S. Prabhakar, S. Bradley, Aiche meeting (2012).
- 554 [3] T. Tran, P. Gripka, L. Kraus, *Petrol.Tech.Q. Catalysis* (2012) 31.
- 555 [4] L. Kellberg, P. Zeuthen, H.J. Jakobsen, *J.Catal.* 143 (1993) 45.
- 556 [5] B. Didillon, A. El Mansour, J.P. Candy, J.M. Basset, F. Le-Peltier, J.P. Boitiaux, *New*
- 557 *Frontiers in Catalysis* 75 (1992) 2371.
- 558 [6] J.M. Britto, M.V. Reboucas, I. Bessa, *Hydrocarbon process* 89 (2010) 65.
- 559 [7] F. Chainet, C.P. Lienemann, M. Courtiade, J. Ponthus, O.F.X. Donard, *J.Anal.At.Spectrom.*
- 560 26 (2011) 30.
- 561 [8] L.N. Kremer, T.G. Hueston, *Petrol.Tech.Q. Summer* (2002) 65.
- 562 [9] C. Rome, T.G. Hueston, *Silicone in the Oil and Gas Industry*.
- 563 [10] G. Camino, S.M. Lomakin, M. Lazzari, *Polymer* 42 (2001) 2395.
- 564 [11] T.H. Thomas, T.C. Kendrick, *J.Polym.Sci., Part A2* 7 (1969) 537.
- 565 [12] G. Camino, S.M. Lomakin, M. Lageard, *Polymer* 43 (2002) 2011.
- 566 [13] J.P. Lewicki, B.P. Mayer, C.T. Alviso, R.S. Maxwell, *J.Inorg.Organomet.P.* 22 (2012) 636.
- 567 [14] S. Hamdani, C. Longuet, D. Perrin, J.M. Lopez-Cuesta, F. Ganachaud, *Polym.Degrad.Stab.*
- 568 94 (2009) 465.
- 569 [15] U.B. Singh, S.C. Gupta, G.N. Flerchinger, J.F. Moncrief, R.G. Lehmann, N.J. Fendinger,
- 570 S.J. Traina, T.J. Logan, *Environ.Sci.Technol.* 34 (2000) 266.
- 571 [16] J.C. Carpenter, J.A. Cella, S.B. Dorn, *Environ.Sci.Technol.* 29 (1995) 864.
- 572 [17] R. Breivik, R. Egebjerg, *Petrol.Tech.Q. Q1* (2008) 69.
- 573 [18] G.V. Smith, S. Tjandra, M. Musoiu, T. Wiltowski, F. Notheisz, M. Bartok, I. Hannus, D.
- 574 Ostgard, V. Malhotra, *J.Catal.* 161 (1996) 441.
- 575 [19] A. Molnar, I. Bucsi, M. Bartok, F. Notheisz, G.V. Smith, *J.Catal.* 98 (1986) 386.
- 576 [20] R.G. Nuzzo, L.H. Dubois, N.E. Bowles, M.A. Trecocke, *J.Catal.* 85 (1984) 267.
- 577 [21] Á. Molnár, I. Bucsi, M. Bartok, *Journal of Molecular Catalysis A: Chemical* 61 (1990) 307.
- 578 [22] R. Sanchez, J.L. Todoli, C.P. Lienemann, J.M. Mermet, *J.Anal.At.Spectrom.* 27 (2012) 937.
- 579 [23] P. Pohl, N. Vorapalawut, B. Bouyssiere, R. Lobinski, *J.Anal.At.Spectrom.* 25 (2010) 1461.
- 580 [24] F. Chainet, M. Courtiade, C.P. Lienemann, J. Ponthus, O.F.X. Donard, *J.Chromatogr.A* 1218
- 581 (2011) 9269.

- 582 [25] F. Chainet, L. Le Meur, M. Courtiade, C.P. Lienemann, J. Ponthus, L. Brunet-Errard, O.F.X.
583 Donard, *Fuel Process. Technol.* 104 (2012) 300.
- 584 [26] F. Chainet, L. Le Meur, M. Courtiade, C.P. Lienemann, J. Ponthus, O.F.X. Donard, *Fuel* 11
585 (2013) 519.
- 586 [27] F. Chainet, L. Le Meur, M. Courtiade, C.P. Lienemann, J. Ponthus, O.F.X. Donard, *Fuel* 116
587 (2014) 478.
- 588 [28] F. Chainet, J. Ponthus, C.P. Lienemann, M. Courtiade, O.F.X. Donard, *Anal. Chem.* 84
589 (2012) 3998.
- 590 [29] F. Chainet, M. Courtiade, C.P. Lienemann, J. Ponthus, O.F.X. Donard, *J. Chromatogr. A* 1264
591 (2012) 80.
- 592 [30] F. Chainet, C.P. Lienemann, J. Ponthus, C. Pecheyran, J. Castro, E. Tessier, O.F.X. Donard,
593 *Spectrochim. Acta, Part B* 97 (2014) 49.
- 594 [31] B. Beguin, Garbowski E., Primet M., *J. Catal.* 127 (1991) 595.
- 595 [32] C.P. Tripp, M.L. Hair, *Langmuir* 11 (1995) 149.
- 596 [33] R.M. Ravenelle, *Heterogeneous catalysts in aqueous phase reforming environments: an*
597 *investigation of material stability. Thèse de Doctorat, Georgia, 2011.*
- 598 [34] S. Mignard, V. Harle, N. Marchal-George EP0955089A1, 1999.
- 599 [35] H. Long, W. Dai, T. Baoliang, P. Hui, T. Guoqi us2012071700, 2012.
- 600 [36] R.-C. Ryan wo9511753, 1995.
- 601 [37] H.-H. Kung, B.-I. Brookes, R.-L. Burwell, *J. Phys. Chem.* 78 (1974) 875.
- 602 [38] K. Arnby, M. Rahmani, M. Sanati, N. Cruise, A.A. Carlsson, M. Skoglundh, *Appl. Catal. B-*
603 *Environ.* 54 (2004) 1.
- 604 [39] M. Rahmani, M. Sohrabi, *Kinet. Catal.* 47 (2006) 891.
- 605 [40] A.C. Larsson, M. Rahmani, K. Arnby, M. Sohrabi, M. Skoglundh, N. Cruise, M. Sanati,
606 *Top. Catal.* 45 (2007) 121.
- 607 [41] S. Tjandra, D. Ostgard, *Catalysis of Organic Reactions* (1992) 137.
- 608 [42] G.V. Smith, S. Tjandra, M. Musoiu, T. Wiltowski, F. Notheisz, M. Bartok, I. Hannus, D.
609 Ostgard, V. Malhotra, *J. Catal.* 161 (1996) 441.
- 610 [43] S. Tjandra, G.V. Smith, M. Musoiu, Notheisz, F. Bartok, M., J. toch, T. Wiltowski, Si
611 modification of Pd and Pt Catalysts, in: *Catalysis of Organic Reactions*, New York, 1995,
612 137–141.

- 613 [44] E.W. Shin, C.H. Choi, K.S. Chang, Y.H. Na, S.H. Moon, *Catalysis Today* 44 (1998) 137.
- 614 [45] E.W. Shin, J.H. Kang, W.J. Kim, J.D. Park, S.H. Moon, *Appl.Catal., A* 223 (2002) 161.
- 615 [46] W.J. Kim, E.W. Shin, J.H. Kang, S.H. Moon, *Appl.Catal., A* 251 (2003) 305.
- 616 [47] Á. Molnár, I. Bucsi, M. Bartók, *Tetrahedron* 48 (1992) 4929.
- 617 [48] J.P. Boitiaux, J. Cosyns, F. Verna, *Stud.Surf.Sci.Catal.* 34 (1987) 105.
- 618 [49] F. Chainet, Silicon speciation in hydrotreatment feeds. Thèse de Doctorat, IFP Energies
619 nouvelles, 2012.
- 620 [50] Á. Molnár, A. Sárkány, M. Varga, *Journal of Molecular Catalysis A: Chemical* 173 (2001)
621 185.
- 622 [51] V. Ponec, G.C. Bond, *Catalysis by metals and alloys: Catalytic hydrogenation and*
623 *dehydrogenation*, Elsevier, Amsterdam, 1995.
- 624 [52] R. Anderson, B. Arkles, G.-L. Larson, *Silicon Compounds: Register and Review*, Bristol,
625 PA, United states, 1984.
- 626 [53] F. Corvaisier, Y. Schuurman, A. Fecant, C. Thomazeau, P. Raybaud, H. Toulhoat, D.
627 Farrusseng, *J.Catal.* 307 (2013) 352.
- 628 [54] N. López, C. Vargas-Fuentes, *Chemical communications (Cambridge, England)* 48 (2012)
629 1379.
- 630 [55] S. Ivanova, B. Louis, B. Madani, J.P. Tessonier, M.J. Ledoux, C. Pham-Huu, *Journal of*
631 *Physical Chemistry C* 111 (2007) 4368.
- 632 [56] L. Piccolo, A. Piednoir, J.-C. Bertolini, *Surface Science* 592 (2005) 169.
- 633 [57] A. Valcarcel, F. Morfin, L. Piccolo, *J.Catal.* 263 (2009) 315.
- 634