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



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

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ABSTRACT

The presence of silicon in petroleum products is a major issue due to its poisoning effect on catalysts. The aim of this work is to combine silicon speciation and poisoning tests. Cyclic siloxanes were the main silicon species found in petroleum products. Other silicon compounds, comprising reactive groups (hydroxy, methoxy and hydroperoxy), were also recovered but at trace levels using GC-ICP/MS. Five well-chosen silicon compounds were used to poison Pd/alumina catalysts. Only dimethoxydimethylsilane poisons Pd-catalysts while polydimethylsiloxane (PDMS) has no effect on their activities in buta-1,3-diene hydrogenation. Unexpectedly, triethylsilane, triethylsilanol and even octamethylcyclotérasiloxane (D_4) exhibit a promoting effect. An interpretation of the phenomena based on various characterizations is proposed.

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RÉSUMÉ

La présence de silicium dans les produits pétroliers est un problème majeur en raison de l'effet poison exercé par cet élément sur les catalyseurs. Le but de ce travail est de réaliser une spéciation du silicium et des tests d'empoisonnement associés. Les siloxanes cycliques sont les composés majoritaires retrouvés dans les produits pétroliers. D'autres molécules silicées, comprenant des groupements réactifs (hydroxy, méthoxy and hydroperoxy) ont également été caractérisées par GC-ICP/MS, mais à l'état de traces. L'impact du silicium sur l'activité en hydrogénation du buta-1,3-diene de catalyseurs Pd supportés sur alumine a été étudié au moyen de cinq espèces silicées choisies en accord avec les résultats de la spéciation. Seul le diméthoxydiméthylsilane a un effet poison. Le polydiméthylsiloxane (PDMS) ne montre aucun effet. De façon inattendue, le triéthylsilane, le triéthylsilanol et également l'octaméthylcyclotérasiloxane (D_4) montrent au contraire un effet promoteur. Une interprétation des phénomènes est proposée sur la base de différentes caractérisations.

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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 an antifoaming additive to avoid the emulsion phenomenon in different processes such as oil recovery, distillation, coking, and 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 reviews on poisoning reported that silicon species can have a very different effect on catalysts depending on the composition of the catalysts [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 effects on catalysts.

In petroleum products, only the 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 of species, trace level concentrations and complexity of gasoline sample, containing around 200 components [24], induce a real analytical challenge to achieve silicon speciation.

More recently, Chainet et al. [25–27] have proposed a methodology combining the production of fresh PDMS degradation products at a high silicon concentration under refining conditions using a pilot plant and the development and application of a multi-technical strategy to characterize silicon species. Different powerful analytical tools (GC/MS in the single ion monitoring (SIM) mode [24], Fourier

transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) [28], heart-cutting gas chromatography coupled to time of flight mass spectrometry (GC-GC/TOFMS) [29] and GC-ICP/MS [30]) were developed using model molecules in solvents and spiked gasolines. PDMS degradation samples were obtained by heating PDMS at 500 °C in a mixture of *n*-heptane/xylene at different residence times and in the presence of steam or not [25]. The innovative analytical strategy was then directly applied to PDMS degradation samples to avoid possible evolution and to be sure that silicon species present when sampling stay in their native form. This global analytical approach is here applied to gasoline samples, containing a very low amount of total silicon, in order to identify the real silicon species present in these feedstocks and potentially identify the ones responsible of downstream catalyst poisoning.

Modification of alumina or of metallic catalysts by silicon species is widely reported in the literature. Various silicon compounds, such as PDMS, tetraorthosilicate (TEOS), siloxane, and silanol, are used to modify the acidic-basic properties of alumina [31,32] or to improve its hydrothermal resistance [33]. Authors agree on a grafting mechanism of these silicon compounds on the alumina surface, converting surface hydroxyl groups to generally hydrophobic Si-containing groups. Siloxane compounds and disilazane compounds are also known to improve the catalytic performance of hydrogenation catalysts [34,35] or hydrotreatment catalysts [36]. Either activity is promoted or deactivation resistance is increased. Some poisoning effects are also reported with these silicon compounds. For instance, silylation with disilazane ($(\text{Me}_3\text{Si})_2\text{NH}$) at 100 °C in an oxygen or hydrogen stream on Pt-based catalysts results in a decrease in activity for hydrogenation of alkenes or alkynes [37]. Also, contacting Pt-based catalysts with hexamethyldisiloxane (L_2) at 350 °C in air results in a decrease in activity for oxidation of volatile organic compounds [38–40]. Several studies also review relationships between catalyst properties and its propensity to be poisoned by silicon species [18,19,41–46]. So, a decrease in the number of metallic sites available for reaction and consequently a decrease in the hydrogenation activity of alkenes, benzene or dienes have been reported for metallic catalysts (Pd, Ni, Pt) supported on silica or on alumina after being contacted with silane compounds, such as silane (SiH_4), triethylsilane (Et_3SiH), tetraethylsilane (Et_4Si) or hexamethyldisilane (Me_6Si_2), under H_2 flow or inert flow and at a high temperature (250 °C). Authors agree on strong interactions between silicon species and catalysts but the nature of metallic surface modification is not yet clearly identified. Either geometric effects due to surface reconstruction [43] or thin overlayers of silicon residues [4] or silicates (Si_xO_y) covering and blocking the surface sites [38–40] or electronic effects [19,46] have been suggested. Smith et al. [18] also studied reactivation of such poisoned catalysts by oxidation and reduction treatment. This reactivation is structure sensitive and catalysts with smaller metal crystallites can achieve a hydrogenation activity greater than the original one.

However, as far as we know, no poisoning study was achieved yet with silicon compounds derivated from PDMS

degradation, especially cyclic siloxanes (D_n), which are the main degradation products, nor in hydrogenation processes operating conditions. This was hampered on the one hand by the absence of knowledge on silicon speciation in the oil and gas industry, and on the other hand by the low amount of silicon in feedstocks and by the presence of other contaminants (sulphur for example) that could hide the real effect of silicon.

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

2. Materials and methods

2.1. Catalysts preparation

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

2.2. Apparatus for poisoning and catalytic tests

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

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

2.3. Poisoning procedure with silicon compounds

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

Several kinds of silicon compounds, presented in Table 1, were considered. The choice of these molecules is discussed in paragraph 3.1. The Si content in *n*-heptane was ranged between 1 wt. % and 3 wt. %. Often in laboratory poisoning tests, a higher poison concentration and shorter exposure time than in industrial units are used [39]. A poisoning procedure was also performed on uncrushed Pd catalysts: after reduction and without any contact with air, catalyst beads are put into a toric basket fitted to the reactor. Samples are named in the following way: X-Y-Z, with X being the catalyst or alumina reference (A, B, A', B'), Y the silicon compound (TESiOH, D_4 , DMDSi, PDMS, TESI) and Z the Si content in the poisoning solution (in wt. %). For example, sample A- D_4 -1 means catalyst A contacted with a 1 wt. % Si solution of D_4 in *n*-heptane.

2.4. Catalytic test

Once the poisoning procedure is completed, the reactor is cooled down to 17°C and about 7 g of buta-1,3-diene are introduced in the liquid phase. Hydrogenation of buta-1,3-diene is run under 10 bar of H_2 , at 17°C and with a high stirring velocity (1600 rpm). Experimental conditions have been previously optimized to avoid mass transfer limitations. The H_2 consumption can be measured accurately by recording the pressure drop inside the hydrogen storage vessel. The reacting mixture is also sampled over time and analysed by gas chromatography coupled to a flame ionization detector (GC-FID). Note that silicon compounds were still present in the reactor during the hydrogenation test but they should not poison the catalyst since the temperature is low and the contact time is very short (tens of minutes) compared to the poisoning procedure. Moreover, it was verified that there is no effect due to the operating conditions of the poisoning procedure on a fresh Pd-catalyst contacted with *n*-heptane only (with no silicon content).

The typical evolution of the H_2 consumption versus time and typical variations of buta-1,3-diene and reaction product concentrations versus time are reported in Fig. 1. Buta-1,3-diene is hydrogenated into butenes (but-1-ene and *cis* and *trans* but-2-enes) and the hydrogenation of butenes into butane only occurs as buta-1,3-diene is completely consumed, as reported in the literature for Pd-based catalysts [47]. Therefore, rate constants were based on the rates of consumption of H_2 for the hydrogenation of buta-1,3-diene into butenes (r_1) and for the hydrogenation of butenes into butane (r_2). Catalyst activity is defined as r_1 and butene selectivity is expressed as the ratio of the consecutive hydrogenation steps (r_1/r_2). The residual activity of the Si-modified catalyst with respect

Table 1

Physical properties of model silicon compounds considered in this work.

Compound	Dihydroxy tetradecamethylsiloxane (PDMS)	Octamethyl cyclotetrasiloxane (D ₄)	Triethylsilane (TESi)	Triethylsilanol (TESiOH)	Dimethoxydimethylsilane (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

to the fresh catalyst is determined according to the following equation:

$$\text{Residual activity (\%)} = 100 \times \frac{r_1(\text{modified catalyst})}{r_1(\text{fresh catalyst})} \quad (1)$$

2.5. Samples

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

Naphtha and pyrolysis gasoline samples, coming from different thermal cracking processes (coking and steam cracking) of various refineries, have been previously

analysed using our multi-technical strategy [24,28–30]. All samples characteristics are detailed in Table 2. Silicon contents in naphtha and gasoline are very low, which makes silicon speciation so difficult. From these samples, naphtha 2 which comes from a steam cracking process was selected to illustrate our approach.

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

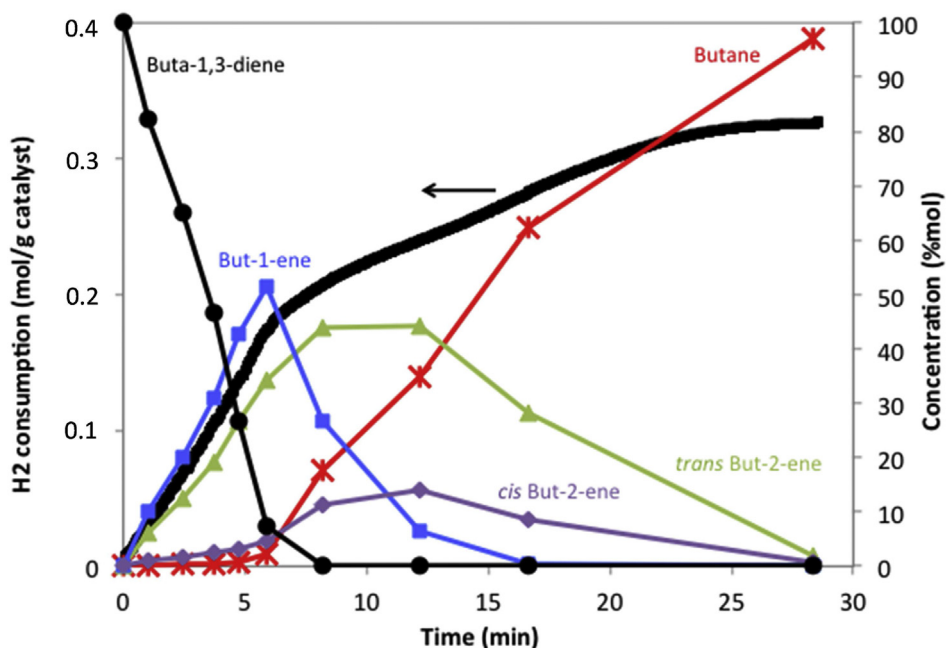


Fig. 1. Hydrogenation of buta-1,3-diene at 17 °C and under 10 bar of H₂ for the fresh Pd-catalyst A. Evolution of the H₂ consumption (large line, left axis) versus time, and evolution of the composition of the mixture of buta-1,3-diene and reaction products (right axis) versus time.

Table 2

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

nd: not determined.

real samples to obtain a better identification of silicon compounds (Table 2).

2.6. Analytical techniques

2.6.1. Characterization of the catalysts

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

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

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

The radial profiles of Pd, Al and Si concentrations along the diameter of the catalyst beads were obtained by Electron Probe Microanalysis (EPMA). The beads were placed in a plastic mould and embedded with a viscous epoxy resin (pre-polymerized in an oven at 70 °C during 20 min). After hardening, the samples were polished in order to obtain a cross section of the beads. The preparations were then coated by a 20 nm thick carbon layer. The measurements were performed with a JEOL JXA 8100 or a Cameca SX100 microprobe, both equipped with five wavelength-dispersive spectrometers. The electron beam conditions were 20 kV acceleration voltage, 200 nA probe current and a focused beam. Pd was measured using the $L\alpha$ -line on a pentaerythritol (PET) crystal, Al and Si using the $K\alpha$ -line on a thallium acid phthalate (TLAP) crystal. The counting times are 40 s on the peaks and 10 s on the backgrounds (measured on each side of the peak). Pure Pd, alumina and silica are used as standards. Such radial profiles were acquired in five different beads.

2.6.2. Characterization of the liquid effluent

The multi-technical approach used for silicon speciation was previously presented in detail for the analysis of the

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

3. Results and discussion

3.1. Identification of real silicon species

Fig. 3 illustrates GC/MS SIM chromatograms obtained for naphtha 2 and PDMS degradation sample. For the naphtha sample, an internal standard (M_4Q) was used for the quantification. This work was previously published by Chainet et al. [24]. Cyclic siloxanes (D_n) are the major silicon species identified both in PDMS degradation samples (about 95% of the total amount of silicon species) and in gasolines (D_3 – D_5). These results confirmed that cyclic siloxanes (D_n) are the main thermal degradation products of PDMS as previously reported in the literature [7,10,12,14]. For the first time, the comparison of real gasoline and representative PDMS degradation sample demonstrates that cyclic siloxanes are the main silicon species in petroleum products at trace levels compared to PDMS degradation samples.

Chainet et al. [26,27] have previously demonstrated that other silicon species (about 5% of the total amount of silicon species), almost never characterized before and present at trace levels compared to cyclic siloxanes, were also present in all petroleum cuts, from the gas fractions to heavy cuts. More than 100 silicon species from 12 chemical families were characterized and possessed reactive functions (hydroxy, methoxy or hydroperoxy) that are able to react very rapidly with the catalyst and potentially cause its deactivation. Scales-up of the GC-ICP/MS chromatograms of the D_5 elution zone for the PDMS degradation sample (a) and naphtha 2 (b) are presented for example in Fig. 4. Using retention indices and MS results for silicon species [27,30], the same three molecules were characterized both in the PDMS degradation sample and in naphtha 2.

According to previous works [28,30,48], a synthesis of the different silicon species characterized only in gasoline fractions (35 °C < boiling points < 200 °C) are detailed in Table 3 and are presented with their number of silicon atoms and identified chemical structure. The three silicon

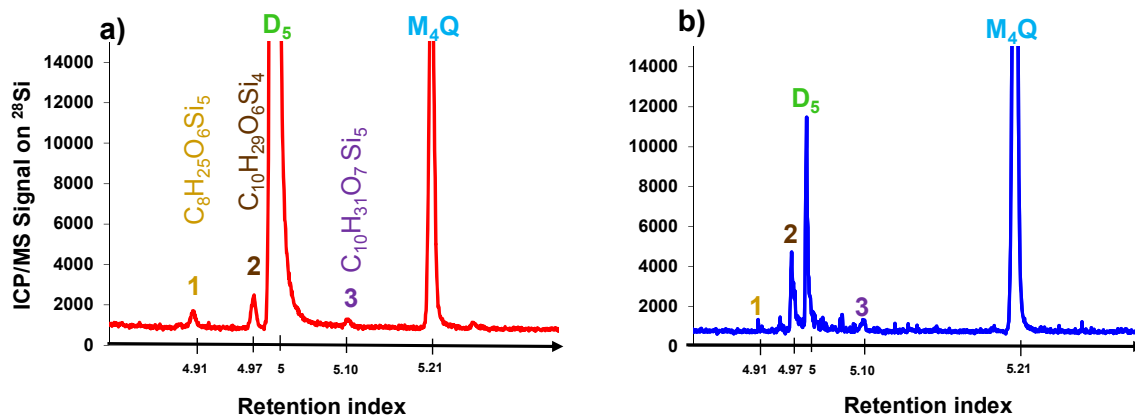


Fig. 4. Scales-up of the GC-ICP/MS chromatograms for the PDMS degradation sample (a) and naphtha 2 (b) illustrating the D₅ elution zone (1: 1,3,3,5,5,7-hexamethyl-2,4,6,8,9-pentaoxa-1,3,5,7-tetrasilabicyclo[5.1.1] nonane (C₈H₂₅O₆Si₅); 2: di(ethoxy methyl) tetramethyl cyclotetrasiloxane (C₁₀H₂₉O₆Si₄);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

compounds (Fig. 4) characterized both in the PDMS degradation sample and in naphtha (Table 3) are also detailed. Except for silanes and α,ω -dihydroxy polydimethylsiloxanes, all silicon species, with various numbers of silicon atoms, were characterized both in PDMS degradation samples and in real gasoline samples using our multi-technical strategy [28,30,48]. These results fully confirmed our approach because same silicon species were recovered between real samples and PDMS degradation samples. Moreover, even if the concentrations of these species in naphtha are obviously very low compared to cyclic siloxanes, we were able to detect and identify them, even in low concentrated real naphthas. Despite their trace level concentrations, these species could have an effect on catalysts considering their reactive functions. In the first part of this work, the representative speciation of silicon allowed us to select the real silicon species formed during refining processes. In the second part, their impact on downstream catalysts will be studied. From all the identified silicon species, five compounds were chosen. These molecules and their characteristics are already presented in Table 1. The selection was made so as to take into account all different chemical forms (cyclic and linear) and possible reactive functions (Si–OH, Si–H, and Si–OCH₃). Practical considerations were also taken into account: commercial availability, ease of use (in liquid phase at ambient temperature) and with a boiling point in the gasoline range (35–200 °C).

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 the fresh catalyst, or a similar, or even a higher

one. From the five silicon compounds used, only DMDSi poisons Pd-catalysts (“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 [19,42–44] have shown a poisoning effect with silane compounds on Pd-based catalysts for diene or alkene or alkyne hydrogenation; however, the 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.

Butene selectivities are also reported in Table 4. The effect on butene selectivity depends on the silicon compound. Butene selectivity is not modified significantly with DMDSi; for the fresh Pd-catalyst as well as for the 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, butene 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 butene selectivity enhancement is obtained with TESI, hydrogenation of butenes being about 15 times slower than hydrogenation of buta-1,3-diene. Whereas butene selectivity degradation seems to be linked with the loss of activity (with DMDSi), selectivity enhancement is linked with the non-modified activity (with PDMS) or promoted activity (with D₄,

Table 3

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)		[48]
Cyclic siloxanes (D ₃ –D ₅)		[24,27–30]	Methyl(methylhydroperoxy) cyclic siloxane (Si ₄ –Si ₅)		[48]
Trimethylsilane		nc	Di(ethoxy methyl) tetramethyl cyclotetrasiloxane ^a (Si ₄)		[48]
Tetramethylsilane			Ethoxy nonamethyl cyclopentasiloxane (Si ₅)		[48]
Trimethylsilanol (Si ₁)		nc	1,3,3,5,5,7-hexamethyl-2,4,6,8,9-pentaoxa-1,3,5,7-tetrasilabicyclo[5.1.1] nonane (Si ₅)		[48]
Dimethoxy tetramethylsilane (Si ₂)		[28]	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)		[48]
Linear polydimethylsiloxanes (L ₂ –L ₅)		[24,29]			

 n is the number of silicon atoms (Si _{n}).

nc: not characterized in real samples.

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

TESiOH, and TESI cases). Such relations between activities and selectivities are reported in the literature on bimetallic catalysts for hydrogenation of alkyne or hydrogenation of dienes [49], even if most of the observations report an activity decrease and a selectivity enhancement [50]. For example, Si-modified Pd catalysts prepared by chemical vapour deposition of triethylsilane exhibit an improved selectivity in alkyne hydrogenation for a given activity [19,43].

3.3. Characterization of Si-modified catalysts

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

3.3.1. Si content in Si-modified catalysts

Si contents in the Si-modified catalysts are reported in Table 4. The Si content in the catalyst depends on the silicon

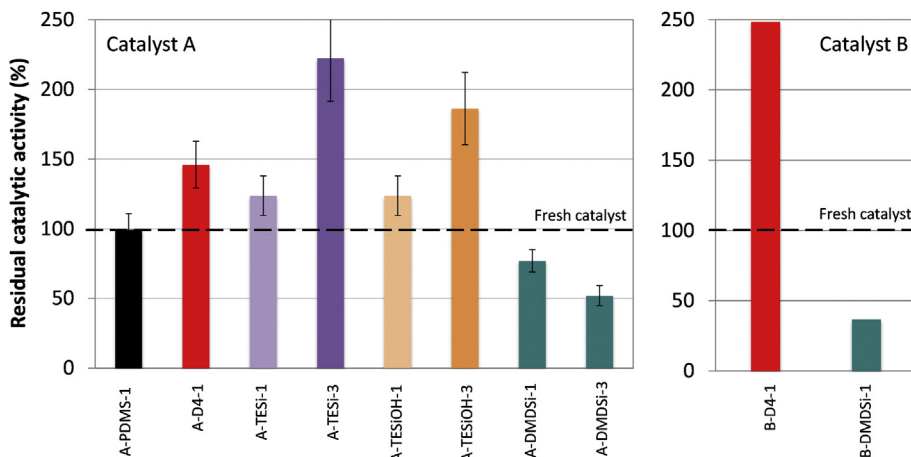
**Fig. 5.** Residual catalytic activities in buta-1,3-diene hydrogenation for Si-modified Pd-based catalysts.

Table 4

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

Sample ^a	Si content in the catalyst (wt. ppm)	Residual activity ($r_1/r_{1, \text{fresh catalyst}}$) (%)	Butene 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 ^b	11,000 ± 220	248 ± 5	nd
B-DMDSi-1	10,942 ± 220	37 ± 6	nd

nd: not determined.

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

^b Poisoning procedure at 70 °C.

compound. For a given catalyst and a given Si content in the poisoning solution, the Si content in the catalyst increases in the following order: TESiOH < DMDSi ≅ D₄ < TESi. Thus, the presence of a Si–H bond in the silicon compound increases Si deposition in the catalyst. This is in agreement with Molnar et al. [21] who correlated the increasing quantity of Si retained on Cu- or Rh- or Pt-supported catalysts and the increasing number of Si–H bonds in the silicon compound (or the decreasing number of Si–C bonds). No relation is observed between the Si content in the catalyst and poisoning or promoting effect: for instance, in catalyst B, with a Si content of about 11,000 wt. ppm, the promoting effect is observed with D₄ and the poisoning effect with DMDSi. It should be noted that the effect (promoting or poisoning effect) is increasing with the Si content.

3.3.2. Silicon deposition

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

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

The Si location inside the support beads was analysed by Electron Probe Microanalysis. For these characterizations, the poisoning procedure was performed on uncrushed Pd catalysts and samples were analysed immediately after the poisoning procedure was completed. As shown in Fig. 7, Si is located everywhere in the support beads, both in the inner core and in the outer shell containing also Pd particles. In the case of D₄ and DMDSi, as Si repartition is homogeneous all along the beads diameter, silicon molecules would appear to be mainly grafted on the alumina surface. Indeed, Si-poisoning experiments that run on bare aluminas show that a large amount of Si is grafted on alumina (Table 6). However, the Si content grafted on the Pd-based catalyst is slightly higher than on bare alumina, which suggests some kind of affinity between Si and Pd particles: additionally to be grafted on alumina surface, silicon molecules can be grafted on the Pd particle surface or grafted on the alumina surface with a higher density at the vicinity of Pd particles. This affinity between Si and Pd particles is much more pronounced in the case of TESi, since the Si content is larger in the outer shell containing Pd particles than in the inner core (Fig. 7b). Si deposition on the Pd particle surface is also indicated by the loss of the Pd surface area recorded on Si-modified catalysts. The Pd surface area, measured by CO chemisorption experiments using a dynamic method, is only 25–35% of the initial surface area of the fresh catalyst, for both TESi-modified catalyst and DMDSi-modified catalyst.

Grafting of silicon species on both alumina support and metallic particles is described also by Rahmani et al. [39,40] while poisoning Pt catalysts with hexamethyldisiloxane (L₂ according to notations in Table 3) at 350 °C in air. They also reported a promoting effect of platinum on deposition of silicon species on the catalyst surface. Kellberg et al. [4] also characterized Si deposits on aged naphtha hydrotreatment (HDT) catalysts by ²⁹Si NMR spectroscopy and described various surface species of modified silica gel. Moreover, Smith et al. [19] reported strongly tri-adsorbed alkyl Si species and even Pd–Si alloy (silicon gradually coats the surface of Pd particles and diffuses into the bulk of the Pd particle) [18,42] after silation by chemical vapour deposition of triethylsilane at 250 °C into flowing hydrogen. Shin et al. [43–45] described a modified Pd surface composed of Pd, Si and SiO₂ obtained after chemical vapour deposition of silane and oxidation at ambient temperature. So, various mechanisms of silicon deposition on metallic supported catalysts can occur depending on poisoning conditions (silicon compound, contact in gas or liquid phase, temperature, reductive or oxidative atmosphere...) and catalyst properties (metallic phase, nature of the support...).

3.3.3. Pd surface area of Si-modified catalysts

As mentioned above, a loss of the Pd surface area is recorded in Si-modified catalysts. This is consistent with the decrease of activity obtained with the DMDSi-modified catalyst (Table 4 and Fig. 7). Such a diminution of the metallic surface area is also described by Smith et al. [18], Shin et al. [43] and other authors [20,37,39,40]. On the contrary, for TESi- and even D₄- or TESiOH-modified catalysts, an increase of activity is obtained despite the decrease of the Pd surface area (Table 4 and Fig. 7). A quite similar

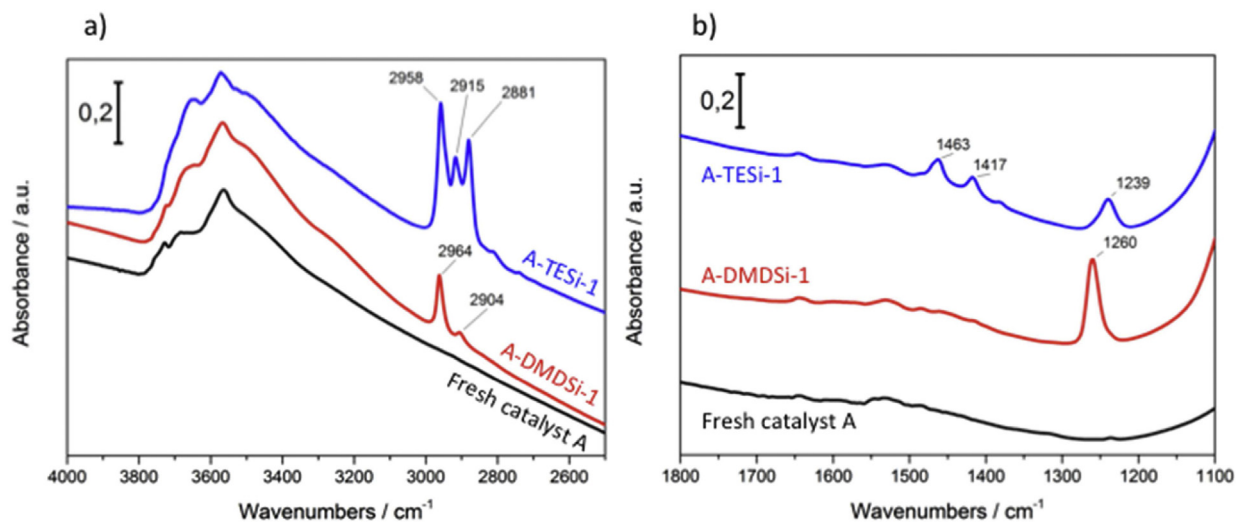


Fig. 6. Scale-up of IR spectra in the 4000–2500 cm^{-1} region (a) and in the 1800–1100 cm^{-1} region (b), for fresh catalyst A and catalyst A modified with DMDSi (sample A-DMDSi-1) and TESi (sample A-TESi-1).

Table 5

Assignment of vibration bands in IR spectra shown in Fig. 6 [51].

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

νCH_n : stretching vibrations of alkyl group CH_n ($n=2$ or 3) – δCH_n : bending vibrations of alkyl group CH_n ($n=2$ or 3) – sym: symmetric – asym: asymmetric.

effect is reported by Rahmani et al. [40] since the Pt catalyst poisoned with L_2 exhibits a high activity in ethyl acetate oxidation despite an important loss of the Pt surface area; different kinds of Pt sites accessible for CO adsorption and for oxidation of ethyl acetate are also mentioned. In our study, the butene selectivity enhancement also observed with these silicon compounds suggests some modification on the electronic and/or geometric properties of Pd particles [49]. Indeed, changing the electronic density of Pd affects the relative adsorption strength of reactants, intermediates and hydrogen and thus catalyst activity and selectivity [52,53]. Alternatively, the presence of strongly adsorbed Si species and of organometallic fragments may block a part of the Pd active surface, which could favour some specific sites, or may modify hydrogen adsorption on Pd, and thus modify selectivity [5,43,54–56]. These effects are more pronounced for the TESi-modified catalyst which presents a higher affinity between Pd and Si, a higher butene selectivity enhancement and a higher activity. Thus, for a given poisoning procedure, silicon compounds with various chemical forms and reactive functions may differ in

their interactions with catalysts, which leads to a more or less noticeable either poisoning effect or promoting effect. This illustrates once more the importance of choosing adequate silicon compounds for laboratory studies. The effects of both a mixture of various silicon compounds and the operating conditions of the poisoning procedure could also be studied.

4. Conclusions

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

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

Si-modified Pd/alumina catalysts were prepared by contacting well-chosen silicon compounds in the liquid phase at moderate temperature and under H_2 pressure. Five silicon compounds were chosen thanks to the previous speciation study, PDMS, octamethylcyclotetrasiloxane (D_4),

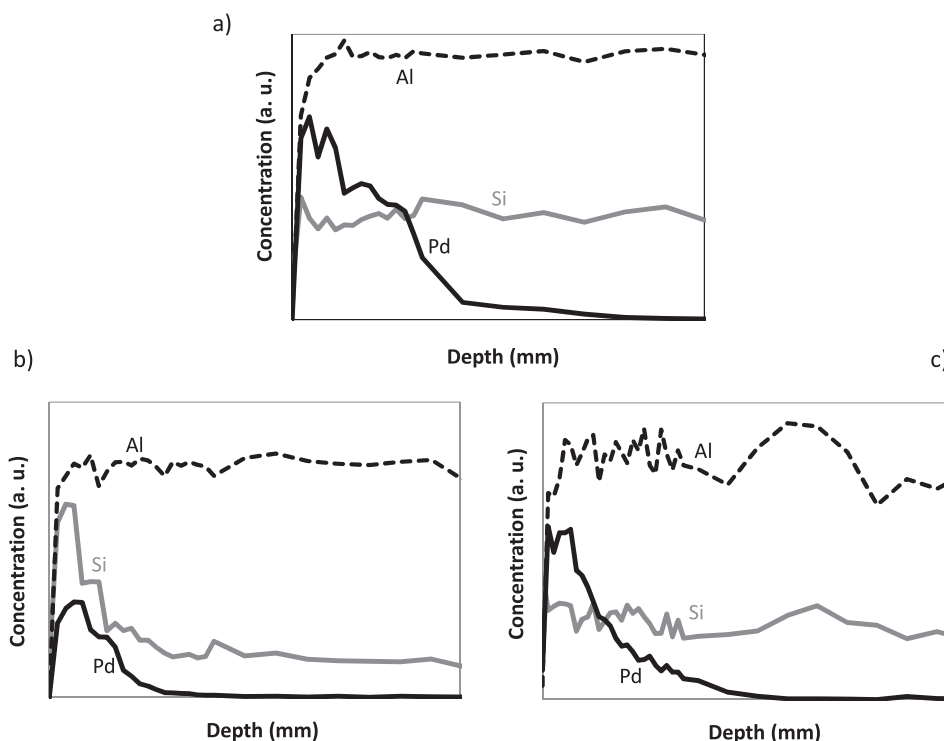


Fig. 7. Metallic repartition profiles for Al, Pd and Si versus support depth (measured by electron probe microanalysis) for catalyst A modified with DMSi (sample A-DMDSi-1) (a) and TESi (sample A-TESi-1) (b), and catalyst B modified with D₄ (sample B-D₄-1) (c).

Table 6

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

Sample	Si content in the catalyst (wt. ppm)
B'-D ₄ -1 ^a	8500 ± 180
B-D ₄ -1 ^a	11,000 ± 220
B'-DMDSi-1	9977 ± 200
B-DMDSi-1	10,942 ± 220

^a Poisoning procedure at 70 °C.

triethylsilane (TESi), triethylsilanol (TESiOH) and dimethoxydimethylsilane (DMDSi), taking into account previously identified chemical forms and reactive functions. Only DMDSi poisoned Pd catalysts while PDMS has no effect on the activity of the Pd catalysts. As silicon is known to act as a severe poison, we expected that cyclic siloxanes (D₄), as the major silicon species in gasolines, poisoned the Pd catalyst. On the contrary, TESi-, TESiOH- and especially D₄-modified catalysts showed a promoting effect on both activity in buta-1,3-diene hydrogenation and butene selectivity. These effects, either promoting or poisoning effects, are more pronounced as the Si content is higher. Silicon molecules are not decomposed during this Si-poisoning procedure, but they are rather grafted on the catalyst, both on the alumina surface and on Pd particles. Combined decreased Pd surface area and enhancement of activity and selectivity suggest some modification on the electronic and/or geometric properties of Pd particles.

These results clearly showed the importance of the representative speciation of silicon in gasoline in order to

study the effect of real species in contact with the catalyst during refining or petrochemical processes. However, despite the poisoning conditions chosen to be as representative as possible for poisoning in industrial units, higher poison concentration and shorter exposure time were used, and care should be taken when extrapolating the results to a real application.

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References

- [1] P. Dufresne, *Appl. Catal. A* 322 (2007) 67.
- [2] M. Serban, M.P. Lapinski, S. Prabhakar, S. Bradley, in: *Proc. 15th Topical on Refinery Processing 2012, Topical Conference on the 2012 AIChE Spring Meeting and 8th Global Congress on Process Safety, Houston, TX, USA, 1–5 April 2012*, pp. 412–419.
- [3] T. Tran, P. Griepka, L. Kraus, *Petrol. Tech. Q. Catal.* (2012) 31.
- [4] L. Kellberg, P. Zeuthen, H.J. Jakobsen, *J. Catal.* 143 (1993) 45.
- [5] B. Didillon, A. El Mansour, J.P. Candy, J.-M. Basset, F. Le-Peltier, J.P. Boitiaux, *New Front. Catal.* 75 (1992) 2371.
- [6] J.M. Britto, M.V. Reboucas, I. Bessa, *Hydrocarb. Process* 89 (2010) 65.
- [7] F. Chainet, C.-P. Lienemann, M. Courtiade, J. Ponthus, O.F.X. Donard, *J. Anal. At. Spectrom.* 26 (2011) 30.

- [8] L.N. Kremer, T.G. Hueston, *Petrol. Tech. Q. Summer* (2002) 65.
- [9] C. Rome, T.G. Hueston, *Silicone in the oil and gas industry*.
- [10] G. Camino, S.M. Lomakin, M. Lazzari, *Polymer* 42 (2001) 2395.
- [11] T.H. Thomas, T.C. Kendrick, *J. Polym. Sci., Part A2* 7 (1969) 537.
- [12] G. Camino, S.M. Lomakin, M. Lageard, *Polymer* 43 (2002) 2011.
- [13] J.P. Lewicki, B.P. Mayer, C.T. Alviso, R.S. Maxwell, *J. Inorg. Organomet.* 22 (2012) 636.
- [14] S. Hamdani, C. Longuet, D. Perrin, J.M. Lopez-Cuesta, F. Ganachaud, *Polym. Degrad. Stab.* 94 (2009) 465.
- [15] U.B. Singh, S.C. Gupta, G.N. Flerchinger, J.F. Moncrief, R.G. Lehmann, N.J. Fendinger, S.J. Traina, T.J. Logan, *Environ. Sci. Technol.* 34 (2000) 266.
- [16] J.C. Carpenter, J.A. Cella, S.B. Dorn, *Environ. Sci. Technol.* 29 (1995) 864.
- [17] R. Breivik, R. Egebjerg, *Petrol. Tech. Q1* (2008) 69.
- [18] G.V. Smith, S. Tjandra, M. Musoiu, T. Wiltowski, F. Notheisz, M. Bartok, I. Hannus, D. Ostgard, V. Malhotra, *J. Catal.* 161 (1996) 441.
- [19] A. Molnar, I. Bucsi, M. Bartok, F. Notheisz, G.V. Smith, *J. Catal.* 98 (1986) 386.
- [20] R.G. Nuzzo, L.H. Dubois, N.E. Bowles, M.A. Trecocke, *J. Catal.* 85 (1984) 267.
- [21] Á. Molnár, I. Bucsi, M. Bartok, *J. Mol. Catal. A Chem.* 61 (1990) 307.
- [22] R. Sanchez, J.-L. Todoli, C.-P. Lienemann, J.-M. Mermet, *J. Anal. At. Spectrom.* 27 (2012) 937.
- [23] P. Pohl, N. Vorapalawut, B. Bouyssié, R. Lobinski, *J. Anal. At. Spectrom.* 25 (2010) 1461.
- [24] F. Chainet, M. Courtiade, C.-P. Lienemann, J. Ponthus, O.F.X. Donard, *J. Chromatogr. A* 1218 (2011) 9269.
- [25] F. Chainet, L. Le Meur, M. Courtiade, C.-P. Lienemann, J. Ponthus, L. Brunet-Errard, O.F.X. Donard, *Fuel Process. Technol.* 104 (2012) 300.
- [26] F. Chainet, L. Le Meur, M. Courtiade, C.-P. Lienemann, J. Ponthus, O.F.X. Donard, *Fuel* 11 (2013) 519.
- [27] F. Chainet, L. Le Meur, M. Courtiade, C.-P. Lienemann, J. Ponthus, O.F.X. Donard, *Fuel* 116 (2014) 478.
- [28] F. Chainet, J. Ponthus, C.-P. Lienemann, M. Courtiade, O.F.X. Donard, *Anal. Chem.* 84 (2012) 3998.
- [29] F. Chainet, M. Courtiade, C.-P. Lienemann, J. Ponthus, O.F.X. Donard, *J. Chromatogr. A* 1264 (2012) 80.
- [30] F. Chainet, C.-P. Lienemann, J. Ponthus, C. Pecheyran, J. Castro, E. Tessier, O.F.X. Donard, *Spectrochim. Acta, Part B* 97 (2014) 49.
- [31] B. Beguin, E. Garbowski, M. Primet, *J. Catal.* 127 (1991) 595.
- [32] C.P. Tripp, M.L. Hair, *Langmuir* 11 (1995) 149.
- [33] R.M. Ravenelle, *Heterogeneous Catalysts in Aqueous Phase Reforming Environments: an Investigation of Material Stability*, PhD thesis, Chemical Engineering, Georgia Institute of Technology, 2011.
- [34] S. Mignard, V. Harle, N. Marchal-George, *European Patent No. EP0955089A1*, 1999.
- [35] H. Long, W. Dai, T. Baoliang, P. Hui, T. Guoqi, *US Patent US2012071700*, 2012.
- [36] R.-C. Ryan *wo9511753*, 1995.
- [37] H.-H. Kung, B.-I. Brookes, R.-L. Burwell, *J. Phys. Chem.* 78 (1974) 875.
- [38] K. Arnby, M. Rahmani, M. Sanati, N. Cruise, A.A. Carlsson, M. Skoglundh, *Appl. Catal. B-Environ.* 54 (2004) 1.
- [39] M. Rahmani, M. Sohrabi, *Kinet. Catal.* 47 (2006) 891.
- [40] A.C. Larsson, M. Rahmani, K. Arnby, M. Sohrabi, M. Skoglundh, N. Cruise, M. Sanati, *Top. Catal.* 45 (2007) 121.
- [41] S. Tjandra, D. Ostgard, *Catal. Org. React.* (1992) 137.
- [42] S. Tjandra, G.V. Smith, M. Musoiu, N.F. Bartok, M.J. Toch, T. Wiltowski, *Si Modification of Pd and Pt Catalysts*, in: M. Scaros, M.L. Prunier (Eds.), *Catalysis of Organic Reactions* [15th Conference], Marcel Dekker, New York, 1995, pp. 137–141.
- [43] E.W. Shin, C.H. Choi, K.S. Chang, Y.H. Na, S.H. Moon, *Catal. Today* 44 (1998) 137.
- [44] E.W. Shin, J.H. Kang, W.J. Kim, J.D. Park, S.H. Moon, *Appl. Catal. A* 223 (2002) 161.
- [45] W.J. Kim, E.W. Shin, J.H. Kang, S.H. Moon, *Appl. Catal. A* 251 (2003) 305.
- [46] Á. Molnár, I. Bucsi, M. Bartók, *Tetrahedron* 48 (1992) 4929.
- [47] J.-P. Boitiaux, J. Cosyns, F. Verna, *Stud. Surf. Sci. Catal.* 34 (1987) 105.
- [48] F. Chainet, *Silicon Speciation in Hydrotreatment Feeds*, PhD thesis, IFP Énergies nouvelles, Lyon & Université de Pau et des pays de l'Adou, Pau, France, 2012.
- [49] Á. Molnár, A. Sárkány, M. Varga, *J. Mol. Catal. A Chem.* 173 (2001) 185.
- [50] V. Ponec, G.C. Bond (Eds.), *Catalysis by Metals and Alloys: Catalytic Hydrogenation and Dehydrogenation*, Elsevier, Amsterdam, 1995.
- [51] R. Anderson, B. Arkles, G.-L. Larson, *Silicon Compounds: Register and Review*, Petrarch Systems, Inc., Bristol, PA, USA, 1984.
- [52] F. Corvaisier, Y. Schuurman, A. Fecant, C. Thomazeau, P. Raybaud, H. Toulhoat, D. Farrusseng, *J. Catal.* 307 (2013) 352.
- [53] N. López, C. Vargas-Fuentes, *Chem. Commun.* 48 (2012) 1379.
- [54] S. Ivanova, B. Louis, B. Madani, J.-P. Tessonnier, M.-J. Ledoux, C. Pham-Huu, *J. Phys. Chem. C* 111 (2007) 4368.
- [55] L. Piccolo, A. Piednoir, J.-C. Bertolini, *Surf. Sci.* 592 (2005) 169.
- [56] A. Valcarcel, F. Morfin, L. Piccolo, *J. Catal.* 263 (2009) 315.