

# Characterization of silicon species issued from PDMS degradation under thermal cracking of hydrocarbons: Part 1 – Gas samples analysis by gas chromatography-time of flight mass spectrometry



Fabien Chainet<sup>a,\*</sup>, Laurent Le Meur<sup>a</sup>, Charles-Philippe Lienemann<sup>a</sup>, Jeremie Ponthus<sup>a</sup>, Marion Courtiade<sup>a</sup>, Olivier François Xavier Donard<sup>b</sup>

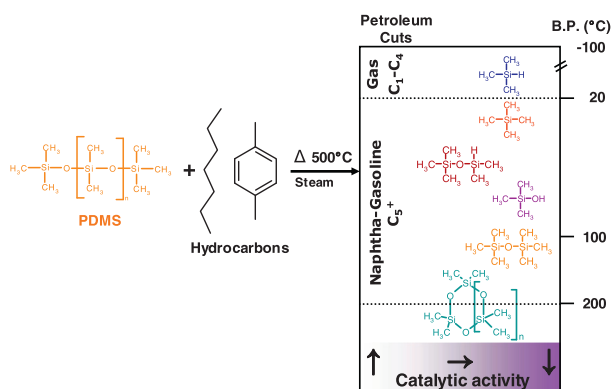
<sup>a</sup> IFP Energies Nouvelles, Rond point de l'échangeur de Solaize, BP3, 69360, Solaize, France

<sup>b</sup> LCABIE-IPREM, UMR 5254, CNRS-UPPA, Helioparc, 2 av. Pr. Angot, 64053 Pau, France

## HIGHLIGHTS

- The understanding of antifoaming degradation is essential for silicon speciation.
- PDMS degradation under thermal cracking of hydrocarbons was achieved.
- Volatile siloxanes, silanes and silanol were characterized by GC/TOFMS.
- A breakthrough in silicon speciation to understand silicon poisoning in gas cuts.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 10 September 2012

Received in revised form 18 March 2013

Accepted 19 March 2013

Available online 10 April 2013

### Keywords:

Hydrocarbons  
Polydimethylsiloxanes  
Thermal degradation  
Gas chromatography  
Mass spectrometry

## ABSTRACT

Silicon species are becoming emergent contaminants in the oil and gas industry due to their severe poisoning effect on the hydrotreatment (HDT) catalysts. Using an experimental pilot plant, fresh and representative samples of PDMS degradation under thermal cracking of hydrocarbons were produced. To follow the evolution of silicon species, the gas fraction was immediately analyzed by GC/TOFMS after the production and also after 4 months of storage at 4 °C. Cyclic siloxanes ( $D_n$ ) as the major products of PDMS thermal degradation were characterized in the gas phase but these compounds are mainly present in the liquid fraction. Five volatile silicon compounds belonging to the families of silanes, siloxanes and silanols were characterized and quantified in the thermal cracking samples depending on the operating conditions applied in degradation tests. Under coking or visbreaking conditions (long residence time, absence of steam), silanes and siloxanes were preferentially formed. Under evaluated steam cracking conditions (short residence time and presence of steam), trimethylsilanol (TMSOH) was mainly produced by the hydrolysis of PDMS. The formation of the linear siloxane ( $L_2$ ) after several month of storage at 4 °C by the self-condensation of TMSOH was also observed. The suspected poisoning effects of these molecules were discussed and could explain the deactivation of catalysts taking place in the refining of the light petroleum cuts. The new identified volatile silicon compounds could affect the performance of the catalyst by the reaction of hydroxyl groups potentially present at the surface of the support with reactive silicon molecules, more specifically silanols.

© 2013 Elsevier Ltd. All rights reserved.

\* Corresponding author. Tel.: +33 4 37 70 24 48; fax: +33 4 37 70 27 45.

E-mail address: [fabien.chainet@ifpen.fr](mailto:fabien.chainet@ifpen.fr) (F. Chainet).

## 1. Introduction

Silicon is probably the most widespread catalytic poison recovered in hydrotreatment feeds [1]. In petroleum products, silicon mainly originates from the use of antifoaming agents such as polydimethylsiloxanes (PDMS) to enhance the crude oil recovery from the reservoir and to avoid the formation of emulsions in the different processes such as coking, visbreaking, steamcracking or distillation [2,3]. Despite of its rather good thermal stability, it degrades around 300 °C [4,5] and generates very different silicon degradation products which can react then with the hydrocarbon matrix. Such degradation processes of PDMS have been studied by Camino et al. [5,6] in a pyrolyser apparatus under inert gas for 2 temperatures of operation 400 °C and 800 °C. Results showed that cyclic siloxanes (D<sub>3</sub>–D<sub>13</sub>) were the major degradation products with traces of linear siloxanes characterized by GC/MS in the liquid fraction. In addition, Fourier transform infra-red spectroscopy (FTIR) showed that at high temperature, CH<sub>4</sub> also forms, likely from Si–Me bond scission. Other siloxane and silane species were not observed in that study.

The literature on poisoning highlighted that silicon species can have a very different effect on the catalytic stage depending on the nature of the catalyst [7], on the experimental conditions [8] but more specifically on the chemical nature of the molecule [8]. Cyclic siloxanes (D<sub>3</sub>–D<sub>6</sub>), resulting from the thermal degradation of PDMS, were previously identified and quantified by GC/MS SIM (single ion monitoring) in naphtha and gasoline samples coming from a steam cracking process [9] but no study was yet reported on the possible poisoning effect of these molecules on HDT catalysts. Silanes, such as TrMS (trimethylsilane) and TMS (tetramethylsilane), were suspected to act as poisons for HDT catalyst stage [10]. Other silanes (SiH<sub>4</sub> [11], CH<sub>3</sub>SiH [12], Et<sub>3</sub>SiH [8,13]) were clearly identified as catalyst poison during hydrogenation or dehydrogenation reactions. On the contrary, an increase of the selectivity of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was observed with (CH<sub>3</sub>)<sub>2</sub>Si<sub>2</sub> [11]. Among siloxane compounds, hexamethyldisiloxane (L<sub>2</sub>) was defined to be the most severe poison for Pd or Pt catalysts when used for the oxidation of volatile organic compounds (VOCs) in a biogas plant [14–17]. To progress on the understanding of silicon poisoning, the chemical nature of silicon species and their relative amount in the different petroleum cuts need to be investigated.

Due to the instability and the reactivity of several silicon compounds [18], the chemical nature of silicon species affecting the catalytic processes can be rather unstable and be modified prior to the speciation analysis achieved in the lab during the storage of the samples. Therefore, this could mean that the previous results reported on silicon speciation in naphtha and gasolines samples were not totally representative of the true silicon species initially present during the catalytic process [9,19]. It is most likely that identified silicon species, after several weeks or months from the initial sampling, could be different from that of the initial silicon molecules possibly affecting the catalytic processes.

To understand the PDMS degradation products under thermal cracking of hydrocarbons and to characterize these silicon species, fresh samples were produced using an experimental pilot plant and were either directly analyzed or carefully stored before further analysis to minimize the evolution of silicon species [20]. A first analytical approach of the silicon species generated under these conditions have been performed and showed that, when using liquid separation by  $\mu$ -SEC-ICP/HRMS, very different silicon compounds occurred over a wide range of molecular masses [20]. For a complete characterization of silicon molecules, the effluents must be analyzed by a multi-technical approach previously developed and using gas chromatography coupled to mass spectrometry in full scan and SIM mode [9] and high resolution mass spectrometry (FT/MS) [19].

In this paper, we present the results obtained on the gas fraction characterization of the PDMS degradation studies. Indeed, the aim of this study is to highlight the volatile silicon compounds, which could affect the performance of HDT catalysts mainly on light petroleum cuts (C<sub>1</sub>–C<sub>4</sub> and C<sub>5</sub><sup>+</sup>). At first, head space (HS) hyphenated to GC/MS was performed to characterize the possible impurities present in the initial PDMS to secure that all characterized silicon compounds would really originate from the thermal degradation. Then, the gas fractions of the five degradation studies previously produced were analyzed by GC/TOFMS using a cryogenic nitrogen (N<sub>2</sub>) valve. The formation of identified and quantified volatile silicon compounds were studied with respect to main critical steps of the process along the different operating conditions focused on the residence time and the steam content. The possible poisoning effect of these volatile silicon molecules were also discussed according to the previous catalytic tests reported in the literature.

## 2. Materials and methods

### 2.1. Silicon standards and solutions

Four volatile silicon compounds were used as reference molecules for this study. These were chosen among a complete mixture used for the speciation of silicon in previous studies [9,19]. Tetramethylsilane (TMS), trimethylsilanol (TMSOH), pentamethyldisiloxane (A) and hexamethyldisiloxane (L<sub>2</sub>) as individual standards were purchased from Sigma–Aldrich (Lyon, France). Acetone of LV-GC grade, especially for trace analysis, was obtained from Biosolve Chemicals (Valkenswaard, Netherlands). A mixture of these compounds at 0.5% in mass in acetone was prepared and different dilutions were achieved. Detection limits (LOD<sub>s</sub>) and linearity of the GC/TOFMS method were evaluated by a direct injection of the liquid standards. The calibration curve was obtained for each silicon standard by GC/TOFMS in order to achieve quantification. The validation of the GC/TOFMS method is presented in Table 2 and further detailed in the Section 3.2. The storage and the complete analytical procedure to avoid silicon contamination were previously defined in Chainet et al. [9,19].

### 2.2. Samples and analytical strategy

The degradation samples of PDMS under thermal cracking of hydrocarbons (heptane and xylene) were produced using a modified pilot plant [20]. The PDMS at 60,000 was purchased from Sigma–Aldrich (Lyon, France). Heptane (AnalaR Normapur, 99.7%) and xylene containing a mixture of the three isomers (ortho, meta and para-xylene) (Purex, 98.5%) were respectively purchased from VWR (Fontenay sous Bois, France) and Carlo-Erba (Val De Reuil, France). A maximum water concentration of 150 ppm was initially present in this mixture and could have an influence during PDMS degradation. All operating conditions are presented in the Table 4. These conditions allowed to determine the influence of the temperature, the residence time and the steam content on the PDMS degradation products. They have been previously discussed in details in Chainet et al. [20]. To simulate a low temperature process in the oil and gas industry and to study the stability of PDMS, the test A was achieved at 250 °C. Four tests were performed under thermal cracking of hydrocarbons at 500 °C. This temperature was considered to be the reference temperature for the majority of the thermal cracking processes such as coking or visbreaking [21]. For a steam cracking process, the temperature is normally set at 800 °C but in our case it was impossible to obtain this temperature without the formation of coke [20]. Due to the design of the pilot plant and the safety conditions needed, the evaluation of the steam

Download English Version:

<https://daneshyari.com/en/article/6640559>

Download Persian Version:

<https://daneshyari.com/article/6640559>

[Daneshyari.com](https://daneshyari.com)