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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 octamethylcyclotetrasiloxane (D_4) exhibit a promoting effect. An interpretation of the phenomena based on various characterizations is proposed.

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 hydropéroxy) 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'octaméthylcyclotétrasiloxane (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 µg/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, silation with disilazane ($(Me_3Si)_2NH$) 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