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# Catalytic oxidation of heavy hydrocarbons over $Pt/Al_2O_3$. Oxidation of $C_{10}^+$ solid hydrocarbons representative of soluble organic fraction of Diesel soots

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ABSTRACT

Oxidation of 20 hydrocarbons (from C10 to C42) representative of soluble organic fraction of Diesel soots were investigated by mixing the hydrocarbon (solid at ambient temperature) with a 0.55 wt%$Pt/Al_2O_3$ catalyst (Pt particle size below 1.2 nm). Oxidation rates were characterized by the temperature of half-conversion ($T_{50}$) and by the quantity of oxygen consumed during the reaction, which allows to determine the amount of the solid hydrocarbon (initially 100 mg of a mixture of 0.133 mmol HC with 2 g of catalyst) actually oxidized during heating in 1%$O_2$/He.

A preliminary study carried out with two selected hydrocarbons showed that turnover frequencies (TOF) are little dependent on the Pt loading. The hydrocarbons should be vaporized before them to react with the Pt catalyst. Ideally, temperatures of light-off and of vaporization should coincide for the optimal transformation into $CO_2$. The molecular structure of the hydrocarbon (number of aromatic rings, $H/C$ ratio, condensed structures, etc.) is a key-parameter for both oxidation and volatility, which explains why a good correlation was observed between $T_{50}$ and boiling temperatures $T_b$. A comparison with light-off tests performed in a stream of gaseous hydrocarbon (vaporized upstream the catalyst) showed that oxidation rates depend on the same structural parameters, except when the hydrocarbon is too volatile (i.e. naphthalene) or, on the contrary, not sufficiently volatile (i.e. n-alkanes in C20-C34). In the first case, a large HC fraction is desorbed without being oxidized while in the second case, oxidation rate is limited by the vaporization.

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## 1. Introduction

Heavy hydrocarbons, especially polycyclic aromatic hydrocarbons (PAH), emitted by automotive engines can cause severe human diseases [1–4] and should be eliminated in catalytic converters [5,6]. Similar technologies are used for VOC abatment in stationary sources (industry, incinerators, etc.) [7,8]. Platinum is the most active metal for total oxidation of most hydrocarbons [9–12], except methane for which palladium is preferred [13–15]. Rhodium is generally less active than Pt and Pd except for olefinic compounds [16,17]. Among the PAH emitted by automotive engines, naphthalene and methyl-1-naphthalene are often chosen as model compounds for testing oxidation catalysts [18–23]. Naphthalene derivatives and heavier aromatics (pyrene, anthracene, fluoranthene) were also investigated as representative compounds in oxidation processes for gas cleanup of incinerators or combustion units [24,25]. In a previous study, the catalytic oxidation of 48 hydrocarbons over a 1%Pt catalyst was investigated [26]. It was shown that the structure of the molecule (number of carbon atoms, degree of branching, presence of C=C double bonds and aromatic rings) were important factors affecting the light-off temperature of the hydrocarbons. In some instances, the formation of oxygenated intermediates may also change the selectivity towards total oxidation. Though oxygenated compounds can be found in exhaust gases of diesel engines, heavy hydrocarbons represent a large part of the organic matter conveyed by the soots [27]. Comparison between PAH analyses in the Diesel fuel and in the exhaust gas seems to show that a significant part of certain PAH are not converted in the engine and survive in the exhaust gas [28]. $^{14}C$ radiolabelled PAH added to the Diesel fuel confirm this hypothesis. The percentage of fluorene and pyrene surviving the combustion is often higher than the fraction of PAH reformed by pyrosynthesis in the engine or the close-to-engine exhaust pipe [29]. The high stability of these PAH demonstrate that their oxidation is difficult even

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in the severe conditions of the engine combustion chamber. In this study, hydrocarbon-air mixtures were injected on the catalyst after vaporization of the hydrocarbon in a saturator. This investigation was limited to HC having a sufficient volatility to get 1500 ppm C in the saturator (alkanes up to C20 and polycyclic hydrocarbons up to C13). For heavier hydrocarbons, this technique could not be applied. Oxidation tests were then carried out using the classical method employed for diesel soot oxidation: the solid hydrocarbon is intimately mixed with the platinum catalyst and light-off profiles are recorded with oxygen only in the gas [30–32].

## 2. Experimental

### 2.1. Catalysts

The condition of the test made that a relatively high sample weight was used for each light-off test. Therefore, it was decided to prepare a less loaded catalyst for the present study. Experiments were carried out on a 0.55 wt%Pt/$Al_2O_3$ catalyst prepared by wet impregnation of a γ-alumina support with an aqueous solution of hexachloroplatinic acid. The support (grain size: 2–4 mm; 105 $m^2\,g^{-1}$; pore volume: 1.18 $cm^3\,g^{-1}$) was crushed and sieved to 0.125–0.250 mm, calcined at 500 °C and impregnated with chlorhydric acid (2%) before Pt impregnation. This chlorination ensures a homogeneous distribution of Pt in the alumina balls. The chlorinated support was dried at 150 °C. After impregnation with hexachloroplatinic acid the catalyst was slowly dried in vacuum at 100 °C (10 h) and then at 150 °C (10 h). The solid was dechlorinated by washing with ammonia (0.1 M) and rinsed with pure water up to pH 7. It was dried again at 100–150 °C and calcined at 500 °C (2 h). No change of textural properties was noticed after Pt impregnation, drying and calcination. Chemical analyses led to the following composition (wt% or ppm): 0.55% Pt; 110 ppm K; 40 ppm Cl; 590 ppm Ca; 260 ppm Fe; 500 ppm Na and 300 ppm Si. The catalyst was finally crushed and sieved to less than 50 μm.

In a preliminary study, the impact of the metal loading (between 0.1 and 1 wt%) was investigated. The low-loaded catalysts were prepared by the same procedure.

The catalysts were characterized by $H_2$-$O_2$ titration in a pulse chromatic apparatus [33]. A dispersion close to 100% was calculated assuming a stoichiometry $H/Pt_S$ and $O/Pt_S$ close to unity. Transmission Electron Microscopy showed very small Pt particles below 1.2 nm.

### 2.2. Light-off tests

The preliminary study on the impact of Pt loading was performed in the saturator reactor described in ref. [28]. All the other experiments were carried out in a soot oxidation reactor. Two grams of 0.55 wt%Pt/$Al_2O_3$ catalyst (50 μm) were physically mixed with 0.133 mmol of hydrocarbon. This ratio corresponds, for instance, to 40 mg coronene in 2 g of catalyst. Temperature-programmed oxidation of 100 mg of this HC/catalyst mixture (6.65 μmol HC) was carried out from ambient temperature to 550 °C at 5 °C $min^{-1}$ in a 1%$O_2$/He mixture (gas flowrate: 20 $cm^3\,min^{-1}$). Oxygen concentration was continuously recorded by catharometry (after trapping of $CO_2$, $H_2O$ and not reacted HC on Zeolite 13X and KOH), which allows to calculate the integrated amount of $O_2$ consumed between 20 °C and $T$°C and the HC conversion at temperature $T$. It is assumed that the oxidation reaction produces only $CO_2$ and water according to eq. (1):

$$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + y/2\,H_2O \quad (1)$$

The amount of HC introduced in the reactor (6.65 μmol) gives the theoretical amount of $O_2$ ($N_{O_2\,th}$) required for total oxidation. The experimental amount of $O_2$ actually consumed between 20 and 550 °C, $N_{O_2\,exp}$, can be compared to $N_{O_2\,th}$, which gives the percentage of theoretical $O_2$ consumed in TPO:

$$\%O_2\,cons = 100 \times \frac{N_{O_2\,exp}}{N_{O_2\,th}} \quad (2)$$

Due to the fact that the hydrocarbon starts to vaporize before it can be oxidized, $N_{O_2\,exp}$ is always smaller than $N_{O_2\,th}$. In this approach, HC conversion is calculated on the basis of $O_2$ consumption profile $N_{O_2}$ vs. $T$. For instance, $T_{50}$ is the temperature at which half of $N_{O_2\,exp}$ has been consumed. Several tests were repeated to determine the interval of confidence of the light-off temperatures. It was concluded that the temperatures at 50% conversion are given at ±5 °C. Oxidation of solid hydrocarbons may also give rise to aldehyde/ketones, etc. or to lighter hydrocarbons (by cracking/dealkylation, etc.). These products were not systematically analyzed but their presence (generally less than a few percents) was evidenced by GC/MS coupling.

## 3. Results and discussion

### 3.1. Preliminary study: influence of Pt loading

Oxidation of *n*-tetradecane and naphthalene was studied under constant HC and $O_2$ concentration at the reactor inlet (1500 ppm C in air, see details in [28]) over four Pt catalysts of variable loading between 0.1 and 1 wt%Pt. All these catalysts were prepared on the same alumina (105 $m^2\,g^{-1}$). $H_2$-$O_2$ titration and electron microscopy showed that metal dispersion was close to 100% for the three less loaded catalysts (0.1 to 0.55%Pt) while it is slightly lower (80%) for the 1 wt% catalyst. The results of the oxidation tests are reported in Table 1. Specific activity and turn-over frequency are virtually constant for the 0.1–0.55 wt% catalysts while they are a little bit greater for the 1 wt% catalyst. This may be ascribed to the moderate increase of particle size in this latter catalyst. Other results (not shown here) have confirmed that HC oxidation was a structure sensitive reaction over Pt, TOF increasing with the particle size. Substituting the 1 wt%Pt catalyst for the 0.55 wt% one increases the light-off temperature by 14 °C when HC oxidation is performed in the saturator reactor (constant concentration at the reactor inlet during the light-off test).

### 3.2. Hydrocarbon oxidation: comparison between the two reaction systems

Catalytic oxidation of some hydrocarbons could be carried out both in the saturator reactor (results in ref. 26, 1 wt%Pt) and in the soot oxidation reactor (present study, 0.55 wt%Pt). Fig. 1 compares the light-off curves recorded in the two reaction systems (N being the name of the hydrocarbon, N corresponds to light-off in the saturator reactor while N-S corresponds to light-off in the soot oxidation reactor). Except for naphthalene, oxidation occurs at higher temperatures in the soot oxidation reactor. The vaporization is an essential step before oxidation. Naphthalene being relatively easy to vaporize, oxidation is not delayed and can occur at low temperature: in the soot oxidation reactor, naphthalene concentration may become very high, which favors a "light-off"-type combustion. Fluorene and hexamethylbenzene having a lower volatility (see Table 2), their oxidation could be delayed up to reach a sufficient concentration in the stream.

### 3.3. Hydrocarbon oxidation in the soot oxidation reactor

Twenty-two hydrocarbons having a number of carbon atoms between 10 and 42 were investigated. Light-off curves for selected HC are reported in Fig. 2 (HC of less than 20 atoms C) and Fig. 3 (HC having 20 atoms C or more). For all the tested hydrocarbons, the

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