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*Highlights (for review)

Catalytic Oxidation of Heavy Hydrocarbons over Pt/Al_2O_3. Oxidation of C_{10}^+ solid hydrocarbons representative of soluble organic fraction of Diesel soots.

Fabrice Diehl, Jacques Barbier Jr, Daniel Duprez*, Isabelle Guibard and Gil Mabilon

Highlights

- Solid hydrocarbons (C20-C42) are representative of soluble organic fraction of Diesel soots
- Oxidation of these hydrocarbons mixed with a Pt catalyst is dependent on their volatility
- Their molecular structure (number of cycles, H/C ratio,…) influences oxidability and volatility in a similar manner
- There is a good correlation between light-off (oxidation) and boiling temperatures (volatility).
- Optimal oxidation process occurs when there is a good fit between these temperatures.

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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.

Fabrice DIEHL[1], Jacques BARBIER Jr[2], Daniel DUPREZ*[2], Isabelle GUIBARD[1]and Gil MABILON[1]

[1] IFP Energies Nouvelles (IFPEN)- Etablissement de Lyon, BP 3, 69360 Solaize, France

[2] Institut de Chimie, des Milieux & Matériaux (IC2MP), Université de Poitiers & CNRS, UMR7285, 4 Rue Michel Brunet, TSA 51106, 86073 Poitiers, France

Short title : Oxidation of Diesel heavy hydrocarbons over Pt

Key-words: Hydrocarbon catalytic oxidation; Diesel oxidation catalysts; Pt catalysts; light-off temperatures; Soluble organic fraction (SOF); Diesel soot; polycyclic aromatic hydrocarbons (PAH); structural effects of hydrocarbon molecules.

*All correspondence should be sent to Daniel Duprez

Tel : (33) +5 49 45 39 98

daniel.duprez@univ-poitiers.fr

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 2g 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 cycles, H/C ratio, condensed structures, …) 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 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.

1. Introduction

Heavy hydrocarbons, especially polycyclic aromatic hydrocarbons (PAH), emitted by automotive engines can cause severe human diseases [1,2,3,4] and should be eliminated in catalytic converters.[5,[6]] Similar technologies are used for VOC abatment in stationary sources (industry, incinerators,…).[7,8] Platinum is the most active metal for total oxidation of most hydrocarbons [9,10,11,12], except methane for which palladium is preferred.[13,14,15] 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.[18,19,20,21,22,23] 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 cycles) 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 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 catalyst and light-off profiles are recorded with air only in the gas.[30,31,32]

2. Experimental

2.1. Catalysts

All the experiments were carried out over a 0.55 wt-% catalyst prepared by impregnation of an alumina support (230 m^2 g^{-1}) with aqueous solution of chloroplatinic acid. Details of the preparation and activation are similar to those used for the 1wt-% catalyst of the previous study [26]. The catalyst was crushed and sieved to less than 50 µm. 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.

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 of 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 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:

$$C_xH_y + (x + y/4)\ O_2 \rightarrow x\ CO_2 + y/2\ H_2O \qquad (1)$$

The amount of HC introduced in the reactor (0.133 mmol) gives the theoretical amount of O_2 (N_{O2th}) required for total oxidation. The experimental amount of O_2 actually consumed between 20 and 550°C, N_{O2exp}, can be compared to N_{O2th}, which gives the percentage of theoretical O_2 consumed in TPO:

$$\%O_2\ \text{cons} = 100 \times \frac{N_{O2exp}}{N_{O2th}} \qquad (2)$$

Due to the fact that the hydrocarbon starts to vaporize before it can be oxidized, N_{O2exp} is always smaller than N_{O2th}. In this approach, HC conversion is calculated on the basis of O_2 consumption profile N_{O2} vs T. For instance, T_{50} is the temperature at which half of N_{O2exp} has been consumed.

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 (230 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). Figure 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 favor 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. The results are reported in Table 2a (hydrocarbons with 10-19 C atoms) and 2b

(hydrocarbons with 20-42 C atoms). For each hydrocarbon, structural (number of C atoms, H/C atomic ratio) as well as physical parameters (melting point T_m, boiling point T_b, enthalpy of vaporization at T_{50}) are reported in the Tables.

Structural parameters are indicative of the number of C-C (or C=C) bonds, of C-H bonds and of the number of aromatic cycles in the molecule while physical parameters represent the ability of the molecule to be vaporized before it to be oxidized. Three kinetic parameters of oxidation are also given: the light-off temperature (T_{50}), the activation energy (determined from the conversion curve *vs* T below 20% conversion), and the % of O_2 consumed calculated by Eq. 2.

3.4. Correlation of light-off temperatures with physical parameters of hydrocarbons

There is no clear correlation between the light-off temperatures and the melting point of hydrocarbons: for instance, hexamethylbenzene and pyrene have similar T_m (168 and 156°C respectively) and very different T_{50} (238 and 320°C respectively); fluoranthene and tetracene have the same T_{50} (319-320°C) and very different T_m (109 and 357°C respectively). The correlation seems much better between the boiling temperature (T_b) and the light-off temperature, which illustrates the crucial role of the hydrocarbon vaporization on its oxidation (Fig. 2). A linear relationship may be drawn whose equation is:

$$T_{50}\ (°C) = 0.553 \times T_b + 95 \text{ for } 200°C < T_b < 525°C \qquad (3)$$

At the lowest boiling temperatures, T_{50} is close to T_b while the hydrocarbons oxidize at 100°C below their boiling temperature for the less volatile compounds.

3.5. Correlation of light-off temperatures with structural parameters of hydrocarbons

Most of the studied hydrocarbons being aromatics, it seemed interesting to correlate the light-off temperatures with the number of aromatic cycles. The results are represented on Fig. 3. If n-alkanes (no aromatic cycles) and naphthalene (very volatile compared to other

hydrocarbons) are excepted, Fig. 3 shows a fairly good correlation between T_{50} and the number of aromatic cycles (Eq. 4):

$$T_{50}\ (°C) = 18.2 \times N + 247 \qquad (4)$$

N being the number of aromatic cycles ($1<N<8$). The deviation between the theoretical values given by Eq. 4 and the experimental values may reach 20-30°C.

The hydrogen content in the molecule may also affect the oxidability of the hydrocarbon. Fig. 4 shows the correlation between T_{50} and the H/C ratio. If *n*-alkanes and hexamethylbenzene are excepted, a linear correlation between T_{50} and H/C ratio can be observed (line [a], eq. 5).

$$T_{50}\ (°C) = 596 - 414 \times (H/C) \text{ for } 0.5<H/C<0.8 \qquad (5)$$

The slope being very high, deviations of about 30-40°C between the theoretical and the experimental values can be obtained.

3.6. Correlation of light-off temperatures with the percentage of O_2 consumed

The percentage of O_2 consumed is a critical factor which determines the fraction of the hydrocarbon really oxidized and not simply vaporized. An attempt was made to correlate the fraction of O_2 consumed with the light-off temperature of the hydrocarbons. The results are represented on the figure 5. As can be seen, a good correlation is observed with the following relationship:

$$T_{50}\ (°C) = 207 + 2.47 \times (\%O_2 \text{ cons}) \text{ for } 2\% < \%O_2 \text{ cons} < 67\% \qquad (6)$$

3.7. Reaction mechanism. Vaporization and oxidation.

From the above correlations, it seems that the reaction proceeds in two steps: (i) first, vaporization of the solid hydrocarbon, (ii) then reaction of the gaseous HC over platinum. For the most volatile compounds (for instance, naphthalene), the second step if the slow step of the whole process: a significant fraction of the hydrocarbon is vaporized but not oxidized. However, the naphthalene concentration becomes very high and the small fraction that is oxidized reacts rather rapidly: the apparent T_{50} is lower than in a saturator reactor delivering a

constant HC concentration. For heavy PAHs, the volatilization plays a major role, which tends to prove that no oxidation can occur if the hydrocarbon is not gasified (see § 3.5). The question arises to know if the rate of hydrocarbon oxidation is only governed by the vaporization step. The whole process of the oxidation in the soot reactor can be depicted in Fig. 6. The solid hydrocarbon is first volatized and the concentration varies exponentially with the temperature (Fig. 6a, branch 1 of curve V). When all the hydrocarbon (0.133 mmol) is volatized, the concentration decreases sharply (branch 2 of curve V). The hydrocarbon is not only vaporized but also oxidized. The conversion rate is represented as a classical light-off curve (Xox in Fig. 6a). Combining the vaporization curve V and the oxidation conversion curve Xox leads to the outlet concentrations depicted in Fig. 6b.

There are two extreme cases: (i) either the hydrocarbon has a relatively high vapor pressure at moderate temperature and can be largely volatized before its oxidation starts (case of naphthalene, see Fig. 5), (ii) or the hydrocarbon is much less volatile and its conversion by oxidation may be significant (case of benzo[ghi]perylene in Fig. 5). The oxidation rate of solid hydrocarbons is thus strongly related to their volatility. As suggested by the good correlation between T_{50} and boiling temperatures for PAH molecules (Fig. 2), it seems that the molecular structure would have similar effects on both oxidability and volatility. The number of aromatic cycles and the H/C ratio (linked to the degree of condensation of the cycles) are parameters representing at the best the T_{50} and the boiling temperatures. The behavior of aerosols containing thousands of organic compounds was recently depicted in terms of molecular structure-physical properties relationship. [34] The vapor pressure of the compounds (as well as the Henry's constant in the case of aerosols) are the main physical parameters allowing to predict the behavior of the organic compounds in the aerosols (including their transformation by different oxidation processes).

To sum up, the molecular structure of PAH may have similar effects on their oxidability and on their volatility and it seems coherent to observe a good correlation between the kinetic of oxidation (T_{50}) and the volatility (T_b). However, conflicting results can be obtained when the volatility is too low, which suggests that the hydrocarbon cannot be significantly oxidized in the solid state. This is the case of normal paraffins whose oxidation rate decreases with the number of carbons in the molecule (Fig. 4). The reverse tendency was observed when the hydrocarbon is vaporized upstream the catalyst.[26] In the later study, the number of carbon atoms in the *n*-alkane was limited to 20 while, here, molecules with 28 and 34 carbon atoms were tested. Change of oxidability of *n*-alkanes for *n*>20 being little likely, the behavior of these heavy compounds is well explained by their insufficient volatility.

4. Conclusions

Oxidation of solid hydrocarbons mixed with a Pt catalyst is strongly dependent on their volatility. Two extreme cases can occur:

- The hydrocarbon is highly volatile : it desorbs before it to be oxidized (case of naphthalene). A great part of the hydrocarbon is not oxidized to CO2 and may participate to the formation of toxic aerosol.
- The hydrocarbon is very little volatile: its desorption limits the rate of oxidation.

For most of the 20 hydrocarbons tested (from C10 to C42), oxidation rates are linked to their molecular structure: highly condensed hydrocarbons, low H/C ratio, number of aromatic cycles are parameters affecting the reactivity. As these parameters also affects the volatility, a correlation between boiling points, temperatures of 50% conversion and molecular structure is evidenced.

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Legends of Tables and Figures

Table 1
Specific activity (per g. of Pt) and turn-over frequency (per Pt site) in oxidation of *n*-tetradecane at 135°C and naphthalene at 205°C. Effect of the platinum loading. The light-off temperature (50% conversion) is given in the last column.

Table 2a
Structure, physical properties and oxidability (T_{50}) of selected C10-C19 hydrocarbons .

Table 2b
Structure, physical properties and oxidability (T_{50}) of selected C20-C42 hydrocarbons .

Figure 1
Comparison between the two reaction systems. Open symbols: oxidation of gaseous hydrocarbons injected upstream the catalyst (1500 ppm C in air; temperature ramp: 5°C min^{-1}; 1wt-% Pt/Al_2O_3; see ref. [26]). Filled symbols: oxidation of solid hydrocarbons (100 mg of a physical mixture of 0.133 mmol HC+2g of 0.55 wt-%Pt/Al_2O_3; 1% O_2/He; temperature ramp: 5°C min^{-1}).

Figure 2
Correlation between light-off temperatures (half conversion, T_{50}) and boiling temperatures T_b of the hydrocarbons.

Figure 3
Correlation between light-off temperatures (half conversion, T_{50}) and number of aromatic cycles in the hydrocarbon molecules.

Figure 4
Correlation between light-off temperatures (half conversion, T_{50}) and H/C ratio in the hydrocarbon molecule.

Figure 5
Correlation between light-off temperatures (half conversion, T_{50}) and the faction of O_2 actually consumed by oxidation between 20 and 550°C (see Eq. 2).

Figure 6
(a) Changes of HC concentration [C] during the vaporization process (part ❶: normal increase when the temperature increases; part ❷: [C] decrease when all the HC is vaporized). Dotted line: theoretical HC conversion by oxidation. (b) resulting concentrations of non reacted HC and of CO_2 at the reactor outlet.

Table 1
Specific activity (per g. of Pt) and turn-over frequency (per Pt site) in oxidation of *n*-tetradecane at 135°C and naphthalene at 205°C. Effect of the platinum loading. The light-off temperature (50% conversion) is given in the last column.

Pt loading (wt-%)	Hydrocarbon	Temperature (°C)	Conversion (%)	Activity (mmol/g Pt/s)	TOF (s^{-1})	T_{50} (°C)
0.1	n-C_{14}	135	1.3	1.33	0.26	203
	naphthalene	205	1.2	1.22	0.24	268
0.24	n-C_{14}	135	3.3	1.38	0.27	183
	naphthalene	205	2.9	1.21	0.24	250
0.55	n-C_{14}	135	7.4	1.34	0.26	170
	naphthalene	205	6.7	1.21	0.24	229
1	n-C_{14}	135	15.3	1.52	0.37	156
	naphthalene	205	19.0	1.89	0.46	215

Table 2a

Structure, physical properties and oxidability (T_{50}) of selected C10-C19 hydrocarbons .

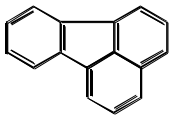
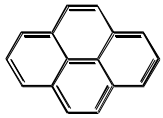
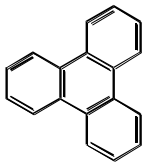
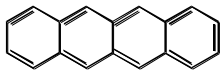
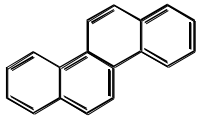
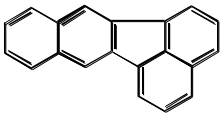
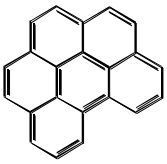
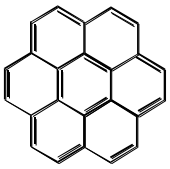
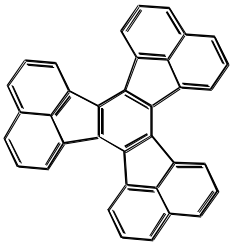
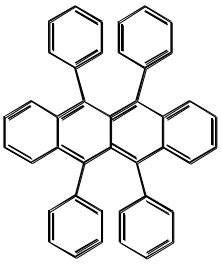
Hydrocarbon	Number of C atoms	T_m °C	T_b °C	H/C atomic ratio	Oxidation reaction			Enthalpy of vaporization at $T=T_{50}$ (kJ/mol)
					T_{50} °C	E_a kJ/mol	$\%O_2$ cons	
Naphthalene	10	80	218	0.80	214	32	2	47
Hexamethylbenzene	12	168	264	1.50	238	38	19	54
Fluorene	13	115	298	0.77	285	18	42	62
9-Fluorenone	13	83	342	0.62	294	12	39	nd
Phenanthrene	14	100	340	0.71	282	12	25	61
 Fluoranthene	16	109	384	0.63	319	33	33	63
 Pyrene	16	156	393	0.63	320	14	34	67
 Triphenylene	18	199	432	0.67	313	29	37	70
 Tetracene	18	357	nd	0.67	320	13	45	144
 Chrysene	18	256	448	0.67	329	24	40	133
Triphenylmethane	19	94	358	0.84	282	14	35	62

Table 2b

Structure, physical properties and oxidability (T_{50}) of selected C20-C42 hydrocarbons .

Hydrocarbon	Number of C atoms	T_m °C	T_b °C	H/C atomic ratio	Oxidation reaction			Enthalpy of vaporization at $T=T_{50}$ (kJ/mol)
					T_{50} °C	E_a kJ/mol	$\%O_2$ cons	
Eicosane (n-C_{20})	20	37	343	2.10	259	11	38	76
 Benzo[k]fluoranthene	20	216	480	0.60	348	13	55	147
 Benzo[ghi]perylene	22	278	>500	0.55	392	17	67	137
 Coronene	24	439	525	0.50	394	10	66	117
Octacosane (n-C_{28})	28	62	nd	2.07	304	14	54	97
Tétratriacontane (n-C_{34})	34	73	nd	2.60	309	11	59	119
 Decacyclene	36	nd	nd	0.47	405	13	61	nd
 Rubrene	42	331	nd	0.67	337	12	63	199
Hexaphenylbenzene	42	455	nd	0.71	348	11	57	202

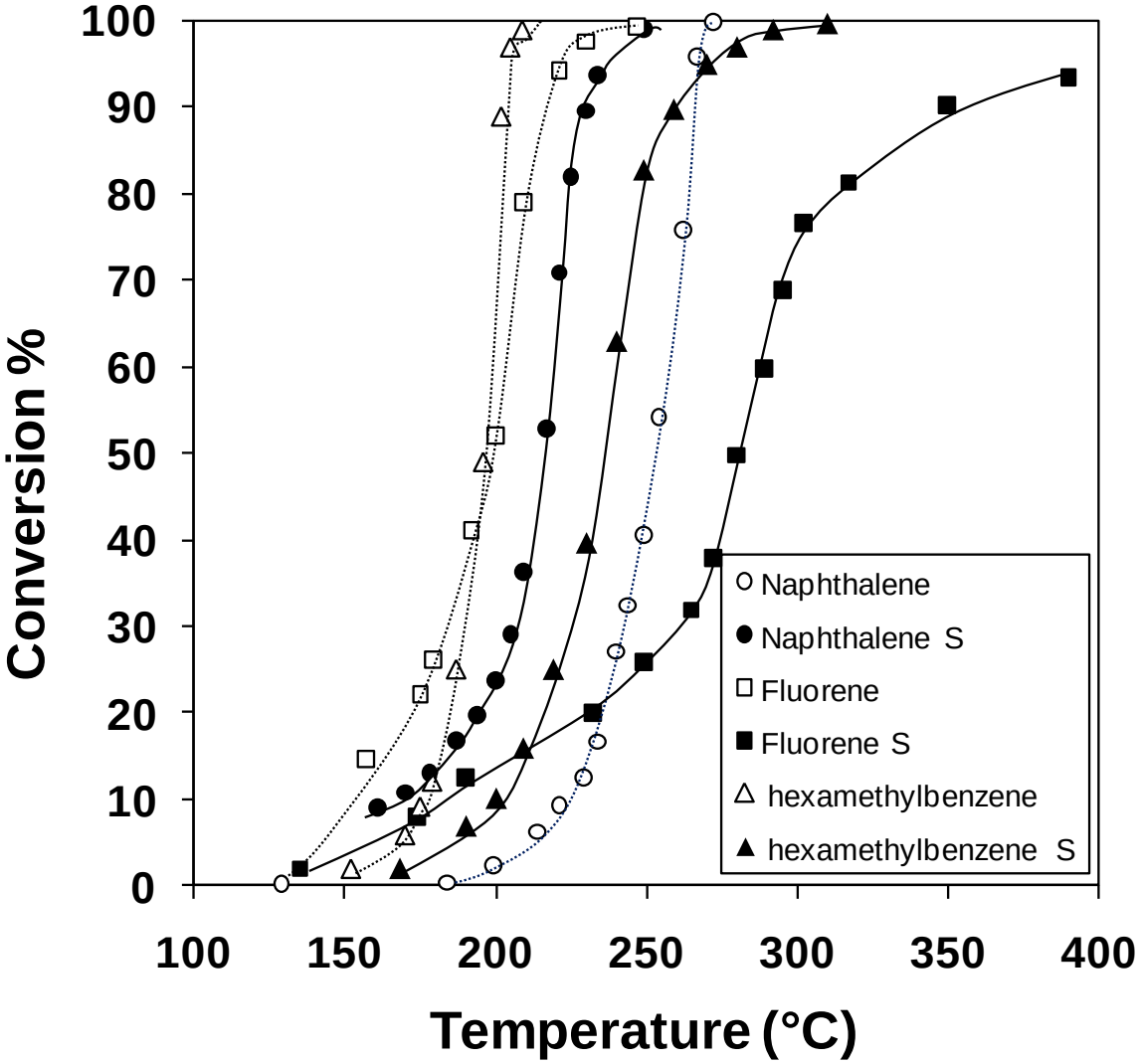


Fig. 1 Comparison between the two reaction systems. Open symbols: oxidation of gaseous hydrocarbons injected upstream the catalyst (1500 ppm C in air; temperature ramp: 5°C min^{-1}; 1wt-% Pt/Al_2O_3; see ref. [26]). Filled symbols: oxidation of solid hydrocarbons (100 mg of a physical mixture of 0.133 mmol HC+2g of 0.55 wt-%Pt/Al_2O_3; temperature ramp: 5°C min^{-1}).

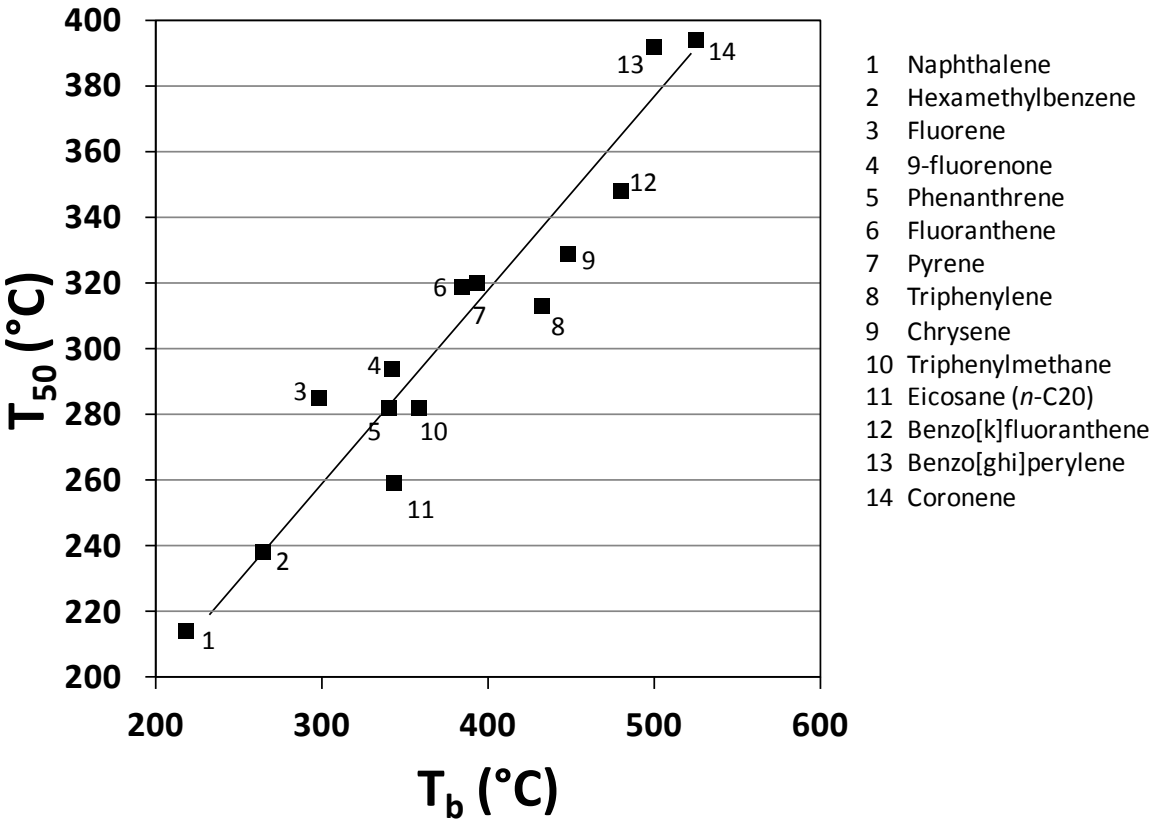


Fig. 2. Correlation between light-off temperatures (half conversion, T_{50}) and boiling temperatures T_b of the hydrocarbons.

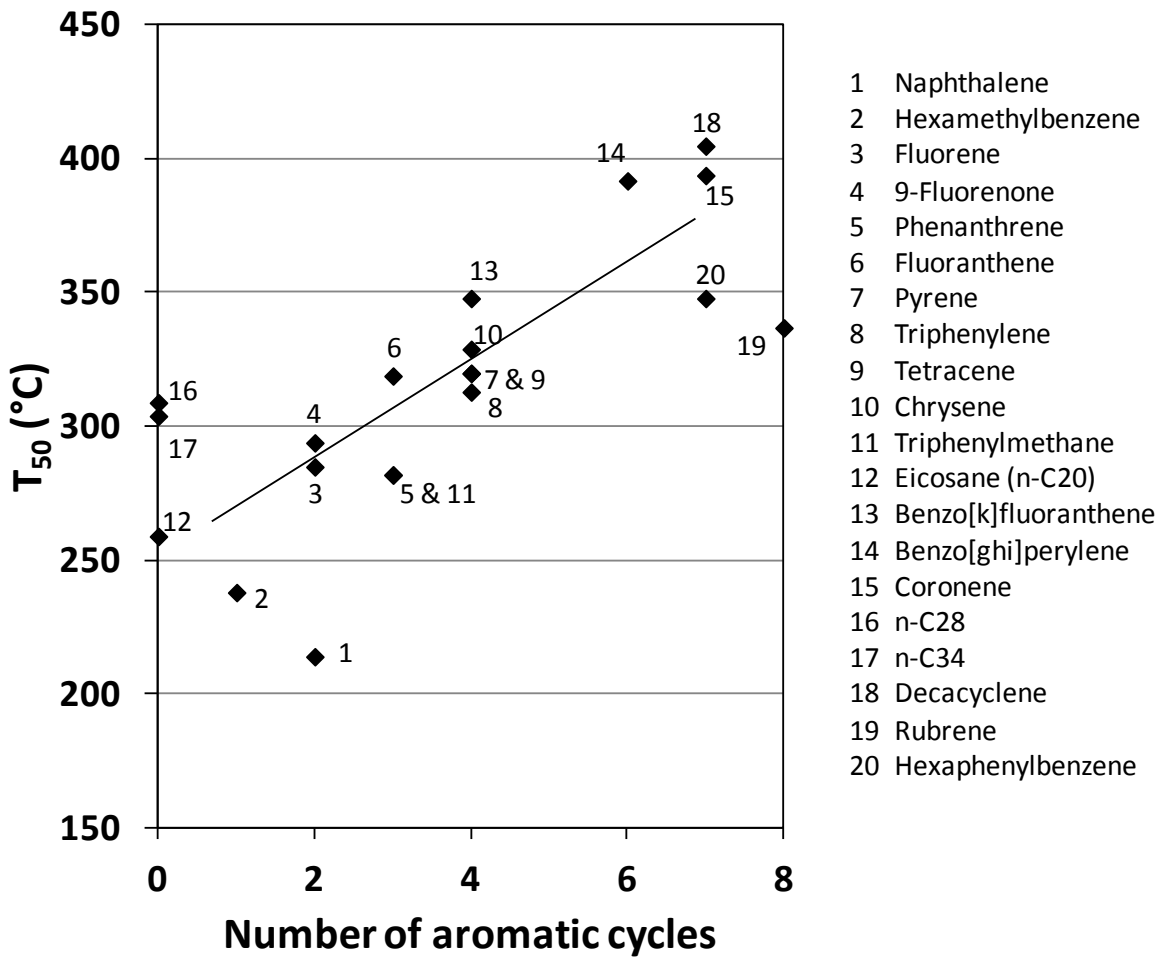


Fig. 3. Correlation between light-off temperatures (half conversion, T_{50}) and number of aromatic cycles in the hydrocarbon molecules.

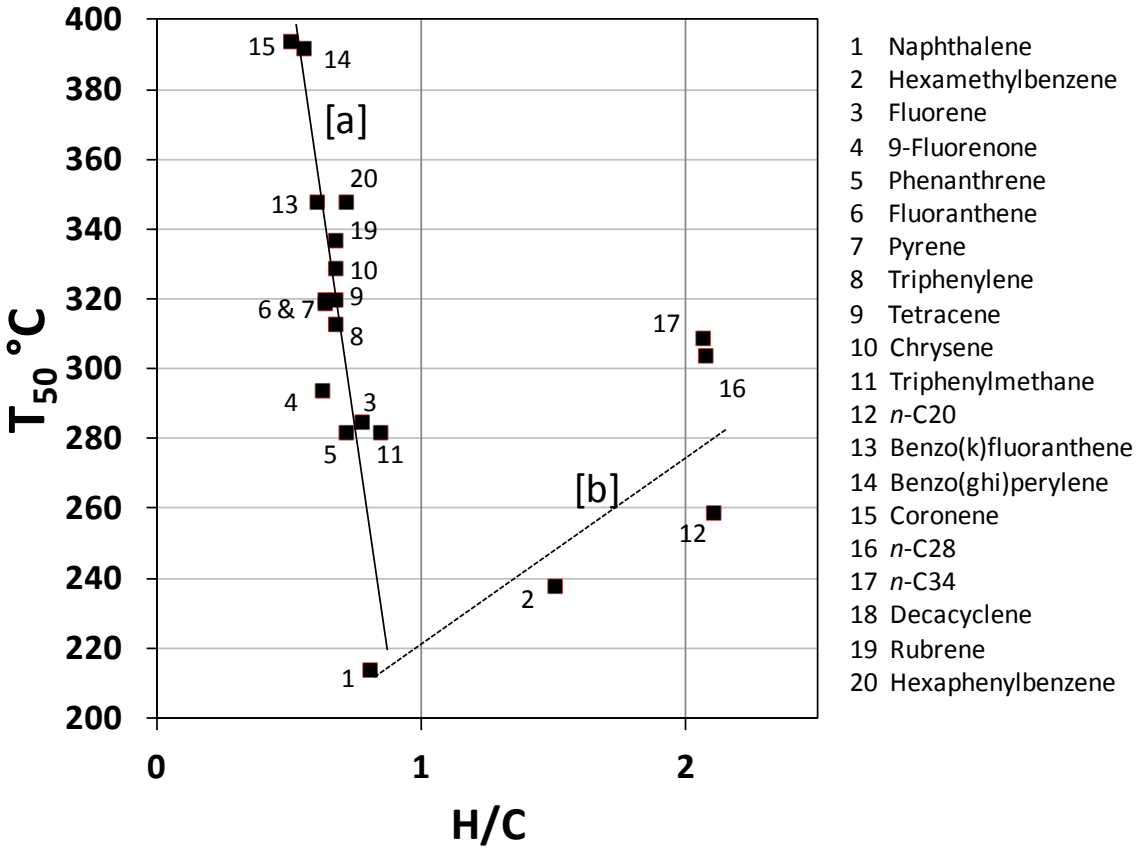


Fig. 4. Correlation between light-off temperatures (half conversion, T_{50}) and H/C ratio in the hydrocarbon molecule.

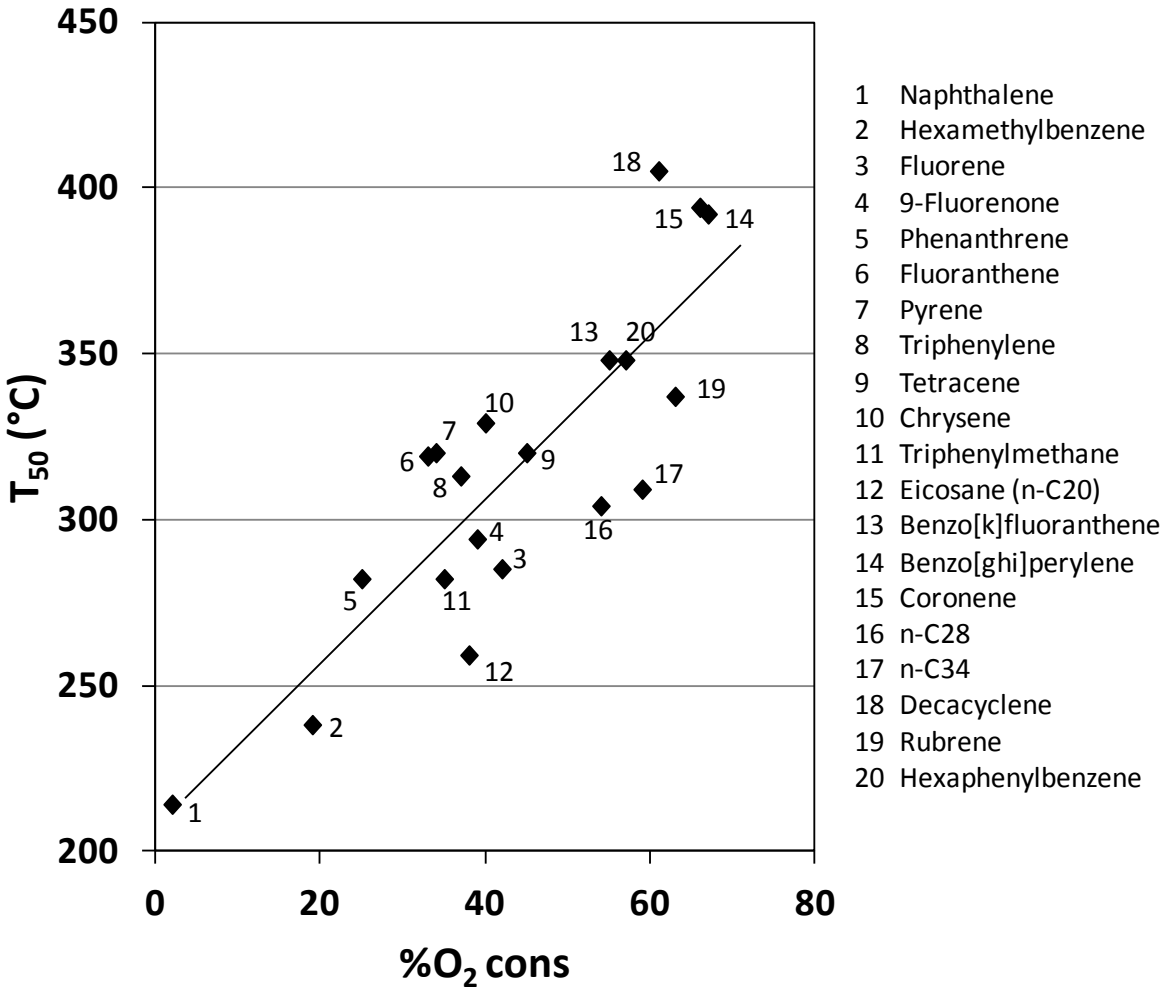


Fig. 5. Correlation between light-off temperatures (half conversion, T_{50}) and the faction of O_2 actually consumed by oxidation between 20 and 550°C (see Eq. 2).

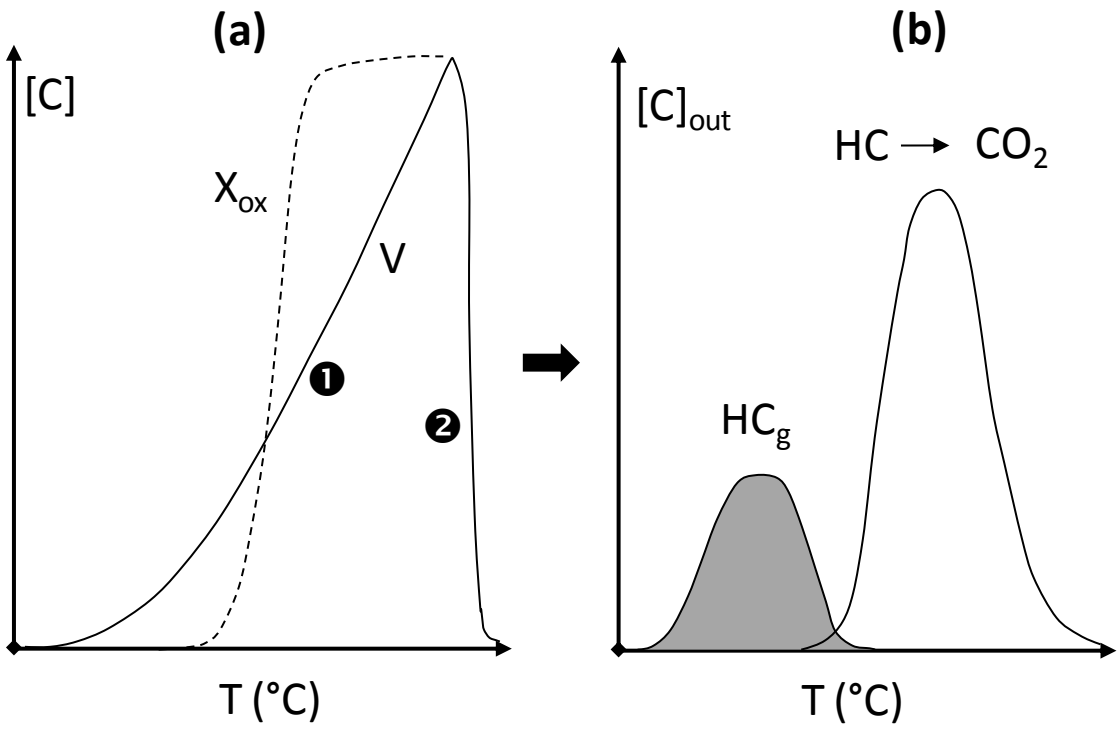


Fig. 6. (a) Changes of HC concentration [C] during the vaporization process (part ❶: normal increase when the temperature increases; part ❷: [C] decrease when all the HC is vaporized). Dotted line: theoretical HC conversion by oxidation. (b) resulting concentrations of non reacted HC and of CO_2 at the reactor outlet.