



Catalytic oxidation of heavy hydrocarbons over Pt/Al₂O₃. Influence of the structure of the molecule on its reactivity

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ABSTRACT

Deep oxidation of 48 hydrocarbons (HCs), from 6 to 20 carbon atoms, was studied over a 1%Pt/Al₂O₃ catalyst (105 m² g⁻¹; mean particle size of Pt: 1 nm). The oxidation reaction (1500 ppm C of HC in air) was carried out by increasing the temperature by step of 5 °C from 100 to 400 °C. The reactivity of HCs was characterized by their *T*₅₀ (temperature at 50% conversion). The reactivity of *n*-alkanes increases with the chain length, following the same evolution with *n* as the ionization potential of the molecule. Isoalkanes are more difficult to oxidize than the corresponding *n*-alkanes. Hydrocarbon reactivity depends on the nature of carbon in the molecule. The ability to be oxidized is greater with C_{II} and C_{III} carbons while C_I and C_{IV} carbons, still more than C_I, are refractory to oxidation. The reactivity of *n*-alkenes depends relatively little on the number of carbons in the molecule. Light alkenes are much more reactive than light alkanes while the reverse can be observed with long-chain hydrocarbons. Contrary to branched alkanes, isoalkenes or cyclenic hydrocarbons are generally more reactive than the corresponding *n*-alkenes. Short side-chain alkylbenzenes (toluene, ethylbenzene, ...) and polymethylbenzenes are more difficult to oxidize than benzene. When the length of the alkyl group is increased, the behaviour of the hydrocarbon in oxidation resembles more and more to long-chain alkanes with a better oxidability. Polyalkylbenzenes with hindered heavy alkyl groups are quite easy to oxidize. The behaviour of bicyclic or tricyclic hydrocarbons is much more complex. Partial or complete hydrogenation increases their reactivity. For instance, oxidability of bicyclic hydrocarbons is in the order: decaline > tetraline > naphthalene. The reactivity of heavier aromatics also depends on their ability to form partial oxidation intermediates (for instance: fluorene to fluorenone) or to possess extremely rigid internal C=C bonds (for instance: acenaphthylene and acenaphthene). These results were discussed in the light of several factors which can affect the reactivity in oxidation: (i) an electron transfer between adsorbed hydrocarbon and adsorbed oxygen species via the surface metal atoms; (ii) the mean C–H bond strength in the molecule and hindrance effects in branched hydrocarbons; (iii) the relative adsorption strength of oxygen and hydrocarbons; (iv) the relative reactivity of hydrocarbons and partially oxidized molecules, intermediates in total oxidation.

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1. Introduction

Heavy hydrocarbons, present as VOC in our environment, are emitted by various sources, mainly incomplete fuel combustion [1], asphalt transformation plants [2] and automotive engines [3–5]. They have a great impact on human health, most of these molecules provoking breathing diseases and cancers [6]. In automotive exhaust gases, they are generally emitted in gas phase or in condensed phase (aerosols) or in adsorbed phase on soot particulates [7]. Due to the high toxicity of heavy hydrocarbons, especially polycyclic aromatic hydrocarbons (PAHs), numerous

studies were performed to get a reliable speciation of these HCs, most often present at a sub-ppm level [8–12]. Heavy hydrocarbon emissions may largely vary depending on origin and nature of fuel [11,13,14], nature of vehicle [11,13,15], engine duty [16–18] and location of gas sampling [15,19]. A recent study also revealed the specific nature of hydrocarbons in transient cycle emissions [20]. A mean composition of heavy hydrocarbons and other organics present in Diesel exhaust gases or adsorbed on soots is given in Table 1. Catalytic oxidation of light alkanes, alkenes and aromatics were widely investigated over noble metal catalysts. Analysis of the pioneering works by Yu Yao [21,22] led to the following main conclusions [23]: (i) platinum is the most active metal in oxidation for virtually all the hydrocarbons except methane, for which palladium is preferred; (ii) light alkanes are difficult to oxidize: the higher the number of carbons in the molecule, the higher the

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Table 1

Mean chemical composition of hydrocarbons and other organics present in Diesel exhaust gases or adsorbed on soots. Total amounts: 30–100 ppm C.

Gaseous alkanes (C1–C40)	Aldehydes: <1 ppm C
CH ₄ : 2–6 ppm C	Formaldehyde
C ₂ H ₆ : 2–5 ppm C	Acetaldehyde
C ₃ +: 3–6 ppm C	Acroleine
Heavy alkanes (adsorbed on soots)	Propionaldehyde
nC16: 60 ppbC	Crotonaldehyde
nC17: 200 ppbC	Metacroleine
nC18: 380 ppbC	n-Butyraldehyde
nC19: 420 ppbC	Benzaldehyde
nC20: 320 ppbC	Naphthalenecarboxaldehyde
nC21: 230 ppbC	
nC22: 150 ppbC	
nC23: 50 ppbC	
Alkenes–dienes–alkynes	Ketones
Ethylene: 5–12 ppm C	Acetone
Acetylene: 3–9 ppm C	Xanthone
Propene: 2–4 ppm C	Fluorenone
Butenes < 1 ppm C	Alkylfluorenone
Butadiene: 1–2 ppm C	Acids
Pentenes < 0.5 ppm C	Naphthalenic acid
	Acetic acid
	Benzoic acid
Light aromatics	Others (S and N compounds)
Benzene: 0.5–1 ppm C	Benzothiophene
Toluene: 0.5–1 ppm C	Dibenzothiophenes and
	alkyldibenzothiophenes: <0.5 ppm C
Ethylbenzene: <0.5 ppm C	Carbazole and methylcarbazoles
Xylenes: <0.5 ppm C	Nitro-PAH
PAH	Rest
Naphthalene: 1 ppbC	O ₂ : 5–15%
Methyl-naphthalene: 3 ppbC	N ₂ : 70–80%
Fluorene: 1 ppbC	CO ₂ : 2–12%
Methyl-fluorenes: 10 ppbC	H ₂ O: 1.8–10%
Phenanthrene: 10 ppbC	CO: 100–800 ppm
Methyl-phenanthrenes: 20 ppbC	H ₂ : 30–300 ppm
Dimethyl-phenanthrenes: 3 ppbC	NO _x : 30–600 ppm
Fluoranthene: 2 ppbC	SO ₂ : 5–50 ppm
Pyrene: 1 ppbC	Particulates: 10–140 ppm C
Benzo[a]anthracene: <1 ppbC	
Benzo[b]fluoranthene: <1 ppbC	
Benzo[a]pyrene: <1 ppbC	

oxidation rate over Pt; (iii) alkenes, aromatics and alcohols are relatively easy to oxidize; (iv) light alkane oxidations are very sensitive to particle size of platinum, big particles being more active than small ones: for instance, turnover frequency in C₃H₈ oxidation at 250 °C over Pt/Al₂O₃ would increase from 0.16 s⁻¹ for 1 nm particles to 1.5 s⁻¹ for 12 nm particles and even to 10 s⁻¹ over Pt foil. In the last three decades, numerous studies were carried out confirming qualitatively these conclusions. The same ranking of activity was also obtained over commercial Pt-Rh/CeO₂-Al₂O₃ monolith catalysts under real conditions with CO, NO, H₂O and CO₂ in the feed [24]. Light-off curves reported by these authors show that the temperatures for a 50% conversion were: methane, 515 °C > ethane, 435 °C > propane, 290 °C > hexane, 195 °C for alkanes, acetylene, 285 °C > ethylene, 205 °C > propene, 185 °C for alkene–alkynes, o-xylene, 225 °C > toluene, 220 °C > benzene, 205 °C for aromatics and n-butanol, 210 °C > n-propanol, 205 °C > ethanol, 200 °C > methanol, 195 °C for alcohols. General reviews on Volatile Organic Compounds (VOC) abatement confirmed Pt to be an excellent catalyst in VOC combustion [25,26]. Though oxidation of C1–C8 compounds was studied in detail, that of heavy hydrocarbons was more rarely investigated [27–29]. Heavy hydrocarbons were also studied as model compounds for the catalytic regeneration of particulate filters by fuel-borne catalysts like ceria [30,31] or for catalytic incinerators [32,33]. In these studies, naphthalene or methyl-1-naphthalene are generally used as model hydrocarbons of PAH [34,35]. The objective of this paper is to investigate the catalytic

oxidation of a great number of heavy hydrocarbons over a Pt/Al₂O₃ catalyst. These HCs were selected among those listed in Table 1, often detected in Diesel exhaust gases. For each family of hydrocarbons, a relationship between their molecular structure and their reactivity will be tentatively established.

2. Experimental

2.1. Catalyst

Most experiments were carried out on a 1 wt% Pt/Al₂O₃ catalyst prepared by dry impregnation of a γ -alumina support with aqueous solution of hexachloroplatinic acid. The support (grain size: 2–4 mm; 105 m² g⁻¹; pore volume: 1.18 cm³ 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 grain. The chlorinated support was dried at 150 °C. Aliquot volume of concentrated solution of hexachloroplatinic acid (25 wt%) was diluted in the exact volume of water to fill in the pore volume. Preliminary tests showed that the pore volume of alumina (1.18 cm³ g⁻¹) could easily be filled with 0.9 cm³ g⁻¹ of aqueous solution. 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) and reduced in H₂ at 450 °C (2 h). No change of textural properties was noticed after Pt impregnation, drying, calcination and reduction. Chemical analyses led to the following composition (wt% or ppm): 0.99% Pt; 110 ppm K; 40 ppm Cl; 590 ppm Ca; 260 ppm Fe; 500 ppm Na and 300 ppm Si.

Platinum accessibility was measured by O₂–H₂ titration at ambient temperature in a pulse chromatographic apparatus [36]. H/Pt₅ and O/Pt₅ stoichiometric ratios were supposed to be equal to unity. A dispersion of 80% was measured by this technique on the standard catalyst calcined at 500 °C and reduced in H₂ at 450 °C. Transmission electron microscopy showed that most Pt particles have a size below 1 nm. Some particles between 1 and 1.6 nm were seen on the TEM pictures. A mean particle size of 0.9–1 nm was calculated in agreement with H₂–O₂ titration.

2.2. Hydrocarbons

About fifty hydrocarbons were selected to represent heavy HC emitted in Diesel exhausts. There may be distributed into three families: alkanes and isoalkanes, alkenes and isoalkenes, aromatics (mono- and polycyclic hydrocarbons). Some tests were also carried out over oxygenated compounds. Hydrocarbons were of purum grade for analysis (99% min) used without any further purification.

2.3. Oxidation reaction. Light-off measurements

The oxidation reaction was carried out in a flow reactor. The catalyst (0.035 g diluted in 2.7 g of α -Al₂O₃) was placed on a porous quartz disk. It was reduced in situ at 500 °C for 2 h in pure H₂ and cooled down to 100 °C in Ar. The hydrocarbon–air mixture was prepared by passing the flow of air (20 cm³ min⁻¹) in a vaporizer whose temperature T_v was maintained constant at ± 0.1 °C. T_v was chosen between –25 and +120 °C so as to obtain a constant hydrocarbon pressure equivalent to 1500 ppm C (i.e. a molar concentration of 1500/n ppm, n being the carbon number in the molecule). The light-off curve was obtained by increasing the oven temperature by step of 5 °C from 100 to 400 °C. After stabilization of the temperature, at least two analyses were carried out and the decision to increase the temperature was taken as soon as the

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