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Applied Catalysis B: Environmental 38 (2002) 139–149

APPLIED CATALYSIS B: ENVIRONMENTAL

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Kinetics of the deep oxidation of benzene, toluene, *n*-hexane and their binary mixtures over a platinum on γ-alumina catalyst

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Received 19 August 2001; received in revised form 24 February 2002; accepted 24 February 2002

Abstract

In this work, the catalytic oxidation of benzene, toluene and *n*-hexane in air, both alone and in binary mixtures, over a commercial Pt on γ-alumina catalyst was studied. Studies have been carried out at concentrations of up to 4200 ppmV, in a laboratory fixed-bed catalytic reactor.

Results for single compounds show that temperature at which 50% conversion is attained (T_{50}) increases as concentration increases for benzene and toluene, while the opposite behaviour is observed for *n*-hexane. Results for mixtures show that, while the presence of *n*-hexane does not affect the conversion of benzene and toluene, the presence of benzene or toluene inhibits the combustion of hexane, and the aromatic compounds inhibits each other when are reacted together.

Results obtained in absence of mass transfer limitations were fit to kinetic expressions: simple Mars–Van Krevelen kinetic expressions for single compounds, and a modified Mars–Van Krevelen mechanism, considering competitive adsorption of the hydrocarbons, for binary mixtures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzene; Toluene; *n*-Hexane; Kinetics; Oxidation; Pt/Al_2O_3 catalyst

1. Introduction

According to one of the most widely accepted definitions, VOC are all organic compounds of anthropogenic nature, different from methane, that can produce photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight [1]. According to this definition, a wide variety of organic compounds, such as aliphatic, aromatic and chlorinated hydrocarbons, aldehydes, ketones, esters, organic acids and alcohols can be considered as VOC. Many substances used in industry are formed or contain VOC: petroleum derivatives, solvents, paints, adhesives, etc. VOC are dangerous for the environment, because of their high volatility and persistence in air, and their ability to travel long distance from their emission points and to be transformed in the atmosphere in other compounds even more dangerous for humans, fauna and flora. For instance, many VOC participate in the formation of photochemical smog, in the greenhouse effect [2], or have been found to be an important cancer risk factor, and to be implicated in neurological problems in urban children [3,4].

The progressive increase of VOC emissions, the information of their hazardous nature, and the resulting increasingly more restrictive environmental regulations in the industrialized countries, have induced the development of different methods for the elimination of VOC [5]. These methods can be classified in two groups: non-destructive and destructive. In the

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PII: S0926-3373(02)00036-X

non-destructive methods, VOC (i.e. from a gaseous emission) are retained, without chemical transformation. Adsorption, absorption or condensation are included in this group. The destructive methods transform VOC into other compounds, inert or less dangerous. Thermal incineration and catalytic oxidation are included in this second group [6]. Selection between different alternatives depends on the nature, flow rate, and concentration of pollutants, outlet required concentration, and other circumstances such as presence of solids or poisons for catalysts, etc.

Catalytic incineration is a technique in which pollutants, usually contained in a gaseous stream, are oxidized completely in the presence of a catalyst. It has the advantages of providing nearly total elimination of pollutants, with no generation of organic by-products at moderate temperatures (approximately 300 °C), hence with low operation cost. Catalytic incineration has been applied, among others, for odour control [7] and treatment of emissions containing evaporated solvents [8,9].

VOC destruction processes are applied often to pollutants in low concentration, so that thermal incineration would require external heating. In these cases, working at low temperature is important in order to improve the economy of the process. For this reason an active and non-selective catalyst, able to transform VOC into deep oxidation products (carbon dioxide and water), is required [8]. There are two types of catalysts used in these processes: oxides of transition metals, and noble metals. It is generally admitted that noble metal catalysts are preferred when there are no poisons (such as sulfur compounds) present, and aromatic compounds are involved in the reaction, because of the low temperatures needed. The noble metals used in practice are Pt and Pd [9,10] usually supported on an oxide (Al_2O_3 or SiO_2), and frequently alloyed with other metals such as Ru, Rh, Os and Ir.

There are many studies on the oxidation of single compounds such as benzene and *n*-hexane on noble metals, including in some cases kinetic studies [11–14]. Most kinetic studies have been carried out at low concentration of the organic compound (less than 1000 ppm), although concentrations much higher can be found often in industrial effluents. Studies on the kinetics of catalytic oxidation of mixtures are much more scarce, and no general model allowing the prediction of the kinetics of mixtures is available, as shown in [8,15–18].

The aim of this work is to study the kinetics of the catalytic oxidation of benzene, toluene and *n*-hexane, both alone and in binary mixtures, over a commercial Pt on γ-alumina catalyst, the mutual influence of the reactants being investigated. Benzene, toluene and *n*-hexane have been chosen as representatives of aromatics and alkanes, because of both the amount of their emissions and their toxicity. Studies have been carried out at concentrations of up to 4200 ppmV, covering a concentration range for which no kinetic studies are available.

2. Experimental

Experiments were carried out in a laboratory fixed-bed catalytic reactor. The catalyst used was dry/reduced 7005 (ESCAT 26), a Pt on γ-alumina catalyst supplied by Engelhard Industries, whose textural characteristics (measured by nitrogen adsorption with a Micromeritics ASAP 2000 apparatus) and composition (given by the manufacturer) are listed in Table 1. Pt was chosen as active metal considering that, according to the literature, it is the most active metal for aromatic structures [19]. In the case of alkanes, Schlangen et al. [20], stated that for those lighter than pentane, Pd is the most active metal, whereas for higher molecular weights, the most active is Pt.

The reactor consisted of a 400 mm length and 9 mm i.d. stainless steel cylinder. Reactor was loaded with 0.30 g of catalyst, crushed and sieved to 250–315 μm, and mixed with 0.60 g of inert alumina (250–500 μm, BASF) where placed in the middle part of the reactor, the upper and lower parts being filled with alumina in extrusions. The reactor was placed inside an electric furnace, temperature being controlled by a PID controller (Honeywell) connected to a thermocouple

Table 1
Chemical and morphological properties of the catalyst used in this work

Platinum loading (%, w/w)	0.5
Support	γ-Alumina
Surface area (BET) (m^2/g)	119
Mesopore volume (BJH desorption) (cm^3/g)	0.49
Average pore diameter (nm)	18.1

situated inside the reactor, that monitored the reaction temperature. The system was provided with five additional thermocouples that measured the reactor wall temperature at different positions. The catalyst was pre-treated in situ by passing air through the reactor heated at 300 °C for 48 h. The absence of catalyst deactivation during a period of 500 h on stream was ensured by periodically taking samples of the reaction product at reference reaction conditions. All the experimental points used for kinetic analysis were duplicated.

The reactor was fed with an air–VOC stream, produced by injecting liquid VOC (Romil, minimum purity: toluene and benzene 99.8%, *n*-hexane 95%), into N-50 synthetic air (Air Liquide) through a Venturi nozzle, to favour evaporation. Air flow rate ($3.5 \times 10^{-5}\,m^3\,s^{-1}$) was controlled by a mass flow controller (Brooks 5850 TR), and the liquid was injected by precision metering pumps (piston, Alltech 325 HPLC, or syringe, Cole Palmer 74900, depending on the flow rate). A scheme of the experimental set-up is given in Fig. 1.

Exhaust gas was analysed by gas chromatography (Hewlett-Packard HP 5890 Series II). VOC in the inlet and outlet streams were analysed using a 30 m fused silica capillary column with apolar stationary phase SE-30, and a FID detector. CO and CO_2 were analysed using a HayeSep N 80/100 and a molecular sieve 45/60 columns connected in series, and a TCD detector. Neither partial oxidation, cracking by-products nor CO have been detected in any experiment, the carbon mass balance fit in all the cases within 2%.

3. Results and discussion

3.1. Study of mass transfer limitations and thermal effects

Preliminary tests showed that no reaction took place in the preheater or catalysed by the reactor walls and inert alumina. Homogeneous reactions started at temperatures higher than 400 °C for the most reactive

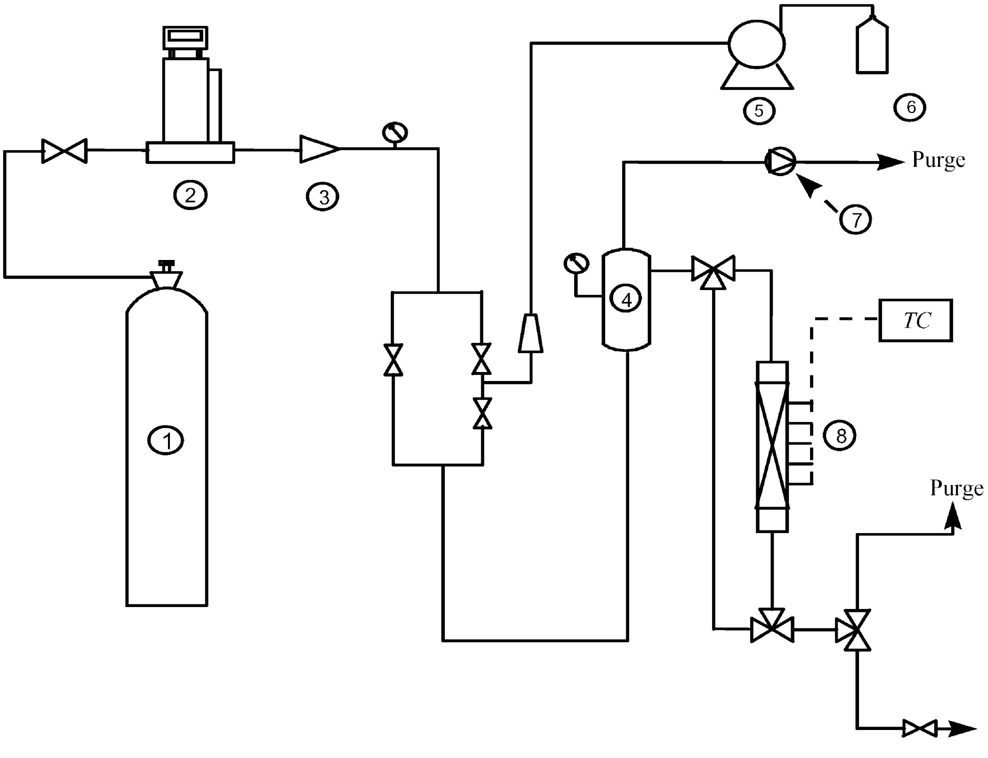


Fig. 1. Schematic diagram of the oxidation reactor: (1) synthetic air cylinder; (2) mass-flow regulator; (3) check valve; (4) damping tank; (5) liquid pump; (6) VOC feed; (7) relief valve; (8) catalytic reactor.

compounds (benzene and toluene). In the experiments carried out in presence of catalyst, total conversion was achieved at 155–160 °C for benzene and 180–190 °C for toluene, whereas temperatures higher than 240 °C were needed for total oxidation of hexane.

Subsequent studies were devoted to ensure the absence of external and internal mass transfer limitations. Internal mass transfer effects were studied by reacting 2000 ppmV benzene with catalyst samples of different average particle diameter (from 100 to 700 μm). It was observed that below 500 μm, the benzene conversion did not depend on the catalyst particle diameter.

External mass transfer effects were checked by obtaining light-off curves working with different total gas flow rates (1.5 and 2.1 nl/min) and hydrocarbon concentrations (2800 and 2000 ppmV), but keeping constant the space time. Results indicate that external mass transfer is not important in all the range of conversions studied.

Thermal effects could be important since the combustion of these compounds is very exothermic (heat of combustion 3267 J/mol for benzene, 3920 J/mol for toluene and 4163 J/mol for toluene), which lead to maximum adiabatic temperature increase (corresponding to 5000 ppmV of each compound) between 550 (benzene) and 705 °C (hexane). In order to check these effects, the experimental test proposed by Kapteijn et al. [21] was performed. According to this test, the influence of thermal effects can be neglected if the addition of different amounts of inert material to the catalyst bed does not affect the conversion. So, light-off curves were recorded for 5000 ppmV toluene (the most exothermic compound at the highest concentration) with different catalyst to inert material ratios (1:1, 1:2 and 1:5). Important differences in the catalyst performance were only observed at very high conversions (> 90%), whereas for T_{50} and T_{10}, differences were always lower than 5%. So it could be concluded that, in spite of the high exothermicity of the reactions, thermal effects are not important, except for very high conversions, due to the low reactor diameter and the relatively high gas velocity used in the experiments.

3.2. Oxidation of single compounds

The behaviour of the different compounds was studied by obtaining light-off curves at different concentrations. Experimental points were obtained both for increasing and decreasing temperatures, no important differences being observed.

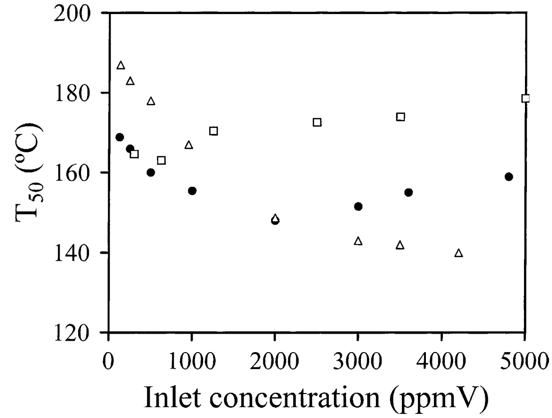


Fig. 2. Evolution of T_{50} with the inlet concentration (ppmV) of benzene (●), toluene (□) and hexane (△).

The reactivity of the compounds studied can be compared in terms of T_{10} and T_{50}, the temperatures at which 10 and 50% conversion are obtained, respectively (both parameters obtained from light-off curves). Results are depicted in Figs. 2 and 3.

In terms of T_{50}, different behaviours were observed for the studied compounds at high and low concentrations. In the case of hexane, T_{50} decreases continuously as hexane concentration increases, while for toluene a slight increase of T_{50} was observed. The tendency found with benzene followed first a decrease

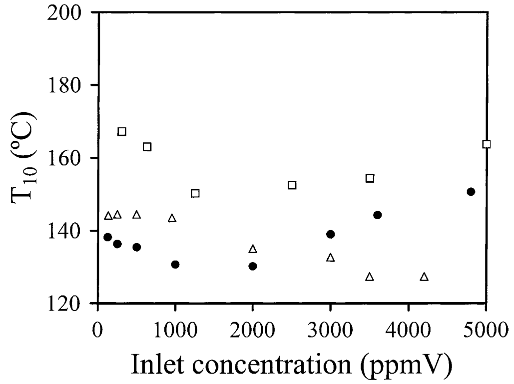


Fig. 3. Evolution of T_{10} with the inlet concentration (ppmV) of benzene (●), toluene (□) and hexane (△).

until 2000 ppm, when T_{50} started to increase. For low concentrations (<1000 ppm), hexane is the less reactive compound, toluene and benzene presenting very similar T_{50}. At higher concentrations, hexane is the most reactive compound (i.e. has the lower T_{50}), followed by benzene and toluene. The behaviour for low concentrations is well reported in the literature, but the behaviour at high VOC concentrations has not been reported so far, to the best of our knowledge. It is important to remark that this behaviour cannot be explained by the thermal effects, since hexane and toluene show very different behaviour at high concentrations, whereas their heat of combustion is very similar.

These results could be explained according to a Langmuir–Hinshelwood mechanism, considering reaction between hydrocarbon and oxygen chemisorbed on the same type of active sites. In the case of hexane, the surface concentration of hexane can be the limiting factor, so higher hexane concentration lead to more hydrocarbon chemisorbed, and hence higher conversions. Results attained with the aromatic compounds suggest that interaction with the catalyst surface for these molecules is stronger, so at higher concentrations the hydrocarbon may compete with oxygen, being then the surface concentration of oxygen the controlling factor. The same explanations also explain the different behaviour of toluene and benzene. The methyl group in the toluene structure increases the electronic density of the aromatic ring (inductive effect), being then the interaction between the molecule and the catalyst surface stronger. So, at low concentrations, when the hydrocarbon surface concentration is the limiting factor, toluene is more active, whereas at higher inlet concentrations, when the oxygen surface concentration is the limiting factor, the inhibition effect of toluene is stronger, and hence the reaction rate of toluene is lower.

This explanation can also justify the differences between our results and that of other authors that compared the reactivity of hexane and aromatics. So, Gangwal et al. [16] observed that the reactivity of hexane was lower, but they worked at lower *n*-hexane concentrations (maximum 500 ppm).

However the explanation for this behaviour is not so clear when considering Mars–Van Krevelen models, which, as will be shown later, are the models that provide better fit to the experimental data. According to these models, the hydrocarbon and oxygen react on different sites. However some electronic or steric factors (less important in lineal molecules such as hexane than in aromatics) could play an important role in the chemisorption.

Some authors [17] claim that T_{10} is a more adequate parameter to evaluate intrinsic reactivities, indicating that at this low conversion thermal effects are not important. As it is observed in Fig. 3, the behaviour for T_{10} is similar to that observed for T_{50}. The most important difference is that toluene presents the highest T_{10} value for all the concentrations studied.

Another parameter used for comparing reactivities is T_{95} (temperature needed to reach 95% conversion). However this parameter, that supplies information about the conditions needed for an effective removal of the pollutant, is strongly influenced by heat transfer phenomena. In our case, no significant trends have been observed, experimental T_{95} values varying between 160 and 190 °C for toluene, 190 and 230 °C for hexane and around 165 °C for benzene.

3.3. Oxidation of binary mixtures

Different binary mixtures of the compounds studied were fed to the reactor (compositions are listed in Table 2), in order to study the inhibitory effects in the oxidation reactions. A total VOC concentration in the range 2000–3000 ppm was used in all the experiments.

Table 2
Binary mixtures studied in the present work (concentrations in ppmV)[a]

Benzene	Toluene	Hexane	Total VOC	T_{95} (°C)
150	2500	0	2650	175.6
1000	1700	0	2700	175.5
1500	1260	0	2760	169.5
2103	755	0	2855	169.7
2700	252	0	2952	170.4
300	0	1800	2100	151.8
1000	0	1413	2413	142.9
1500	0	1000	2500	150.6
2100	0	612	2712	153.1
2700	0	200	2900	155.5
0	2500	204	2704	169.3
0	1763	613	2376	148.8
0	1259	1021	2280	164.1
0	755	1429	2184	147.2
0	252	1838	2090	162.0

[a] T_{95} corresponds to the temperature need for the achieving a total VOC conversion of 95%.

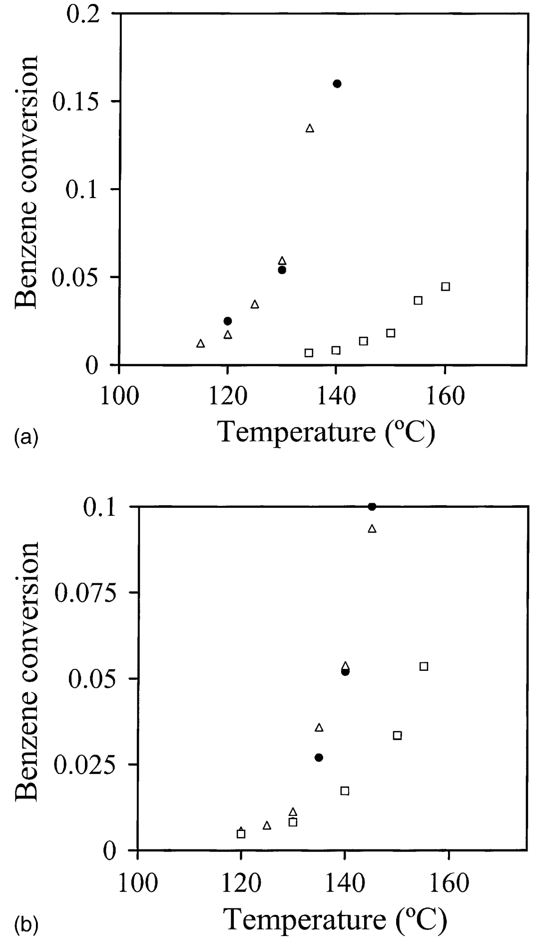


Fig. 4. (a) Evolution of the conversion of 1000 ppmV of benzene alone (●); in presence of 1700 ppmV of toluene (□); 1400 ppmV of hexane (△). (b) Evolution of the conversion of 2700 ppmV of benzene alone (●); in presence of 250 ppmV of toluene (□); 200 ppmV of hexane (△).

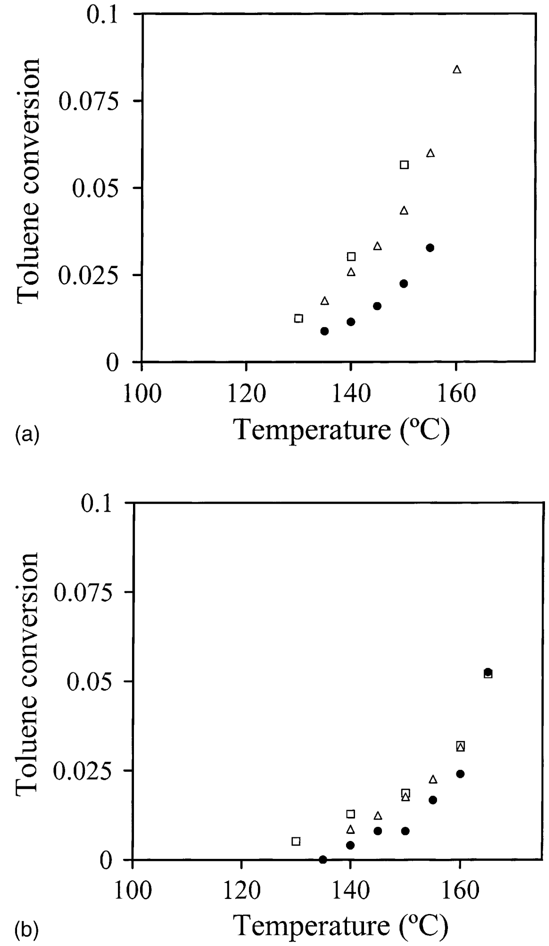


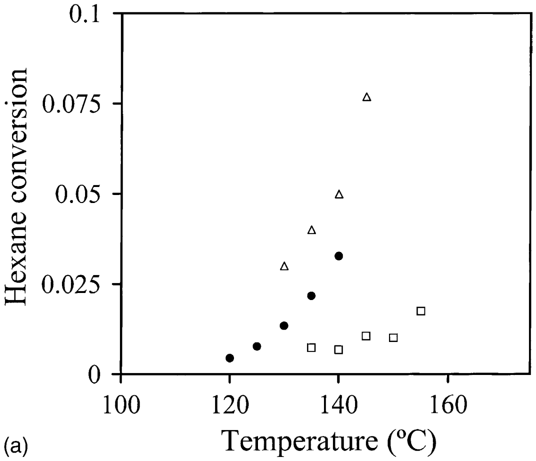
Fig. 5. (a) Evolution of the conversion of 1250 ppmV of toluene alone (□); in presence of 1500 ppmV of benzene (●); 1025 ppmV of hexane (△). (b) Evolution of the conversion of 2500 ppmV of toluene alone (□); in presence of 150 ppmV of benzene (●); 200 ppmV of hexane (△).

Typical behaviours of the mixtures are depicted in Fig. 4 (influence of toluene and hexane in the combustion of benzene), Fig. 5 (influence of benzene and hexane in the combustion of toluene) and Fig. 6 (influence of toluene and benzene in the combustion of hexane). The trends observed in the other experiments (not shown) presented the same trends.

It can be observed that hexane has a negligible effect on the conversion of both benzene and toluene. Similar behaviour was found by Gangwal et al. [16] in hexane–benzene mixtures, and has been observed for saturated organic molecules, even when they contain heteroatoms, such as ethanol [22] or methyl-*tert*-butyl ether [23].

In the case of the aromatic compounds, an important inhibitory effect on the hexane oxidation is observed: hexane conversion decreases markedly when toluene or benzene are present. This behaviour may be qualitatively explained considering the higher affinity of the aromatic compounds for the catalyst surface.

Concerning to the benzene–toluene mixture, important mutual inhibition between both compounds is



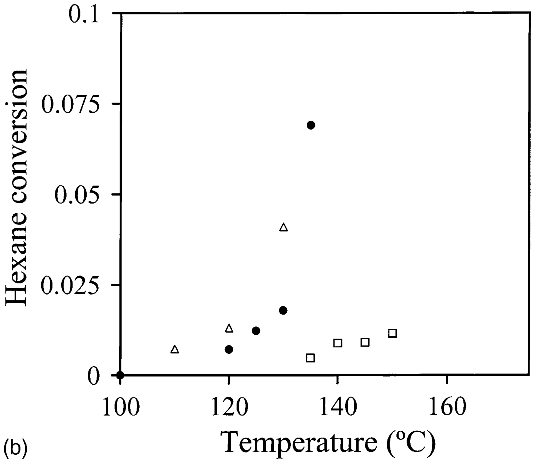


Fig. 6. (a) Evolution of the conversion of 1000 ppmV of hexane alone (△); in presence of 1500 ppmV of benzene (●); 1250 ppmV of toluene (□). (b) Evolution of the conversion of 1800 ppmV of hexane alone (△); in presence of 300 ppmV of benzene (●); 250 ppmV of toluene (□).

observed. Is important to remark that toluene is the compound that inhibits in the highest extension the oxidation of the other VOC, whereas it is inhibited in the lowest extension by the other compounds, whereas benzene oxidation is strongly affected by the presence of toluene and has a lower inhibition capacity than toluene. All these results also suggest that the toluene-surface interaction is stronger than in the case of benzene.

In all the cases discussed here, only low conversions (below 10%) were considered. At higher conversions, there are no remarkable trends in the oxidation behaviour, because conversions rise very fast with temperature to total conversion. Values of T_{95} for these mixtures are shown in Table 2. All the T_{95} values are below 200 °C, and no clear trend is observed.

3.4. Kinetic modelling: pure compounds

Several kinetic models may be used to describe the kinetics of the complete oxidation of pure compounds:

1. *Power-law kinetic expressions*. These are the simplest expressions. These equations can be useful for preliminary designs or comparison purposes, but they do not provide any insight into the reaction mechanism, and usually they are not appropriate to model the behaviour of mixtures [8,24].
2. Kinetic expressions based in mechanisms in which the controlling step is the surface reaction between two adsorbed molecules (Langmuir–Hinshelwood mechanisms), or between an adsorbed molecule and a molecule from the fluid phase (Eley–Rideal mechanisms). A mechanism of the last type was used by Saracco et al. [25] for the oxidation of methane over perovskite catalysts.
3. Two-stage redox models. These models are based on the assumption of a constant oxygen surface concentration on the catalyst, with reaction occurring by interaction between a molecule of reactant and an oxidised portion of the catalyst [26,27]. So, these models postulate two redox steps:
   (a) Reduction of the oxidised catalyst by the hydrocarbon:

$$\text{Cat-O} + \text{R} \overset{k_R}{\to} \text{Cat} + \text{CO}_2$$

   (b) Oxidation of the catalyst by oxygen from the gas phase:

$$2\text{Cat} + \text{O}_2 \overset{k_O}{\to} 2\text{Cat-O}$$

In steady-state operation, the rates of the oxidation and reduction steps must be equal, considering the overall stoichiometry of the reaction (ν). These models are usually preferred for complete oxidation of hydrocarbons over metal oxide and supported Pd catalysts [19,23]. This model has been widely used also for Pt catalysts [17,18,28], although there are not experimental evidences of the presence of oxidised

Pt species in these catalysts. The cited references suggest that the step (b) is a non-equilibrium dissociative adsorption of oxygen, rather than a real oxidation of the catalysts. In this way, step (a) would be the reaction of the hydrocarbon with chemisorbed oxygen. This mechanism leads to the same equation than the Mars–Van Krevelen mechanism, although the meaning of the kinetic parameters is different.

Models of types (2) and (3) were fit to the experimental data. Eley–Rideal models considered both chemisorption of oxygen or hydrocarbon, and Langmuir–Hinshelwood models considered chemisorption of oxygen and hydrocarbon both on different or analogous active sites. As only conversions below 10% were considered in the kinetic analysis, the reactor was considered as differential.

The dependence of the kinetic parameters with temperature was considered to follow an Arrhenius law (kinetic constants) or a Van't Hoff law (adsorption constants). An exponential term appears in both cases, leading to an increase of the non-linear character of the regression, and causing important computational problems in the numerical fit. In order to reduce these problems, resulting form the strong correlation between pre-exponential and exponential parameters, a re-parametrization of these parameters was performed, according to the criteria of Mezaki and Kitrell [29].

The objective function was the summation of the squares of the differences between the calculated and experimental reaction rates, that was minimised using the Powell algorithm [30], implemented in the commercial program Micromath Scientist.

The best results for the three compounds studied were obtained with the Mars–Van Krevelen model, according to which the reaction rate $(-r)$ is given by:

$$(-r) = \frac{k_o k_r p_r p_{O_2}}{k_o p_{O_2} + \nu k_r p_r} \tag{1}$$

where ν is the stoichiometric coefficient for the total combustion reaction (mol O_2/mol of hydrocarbon), p_r and p_{O_2} partial pressures of hydrocarbon and oxygen, respectively, k_o the kinetic constant for the non-equilibrium dissociative adsorption of oxygen on the catalyst surface, and k_r kinetic constant for the reaction between chemisorbed oxygen and the hydrocarbon. Both kinetic constants follow an Arrhenius dependence on temperature:

$$k_o = k_{oo} \exp\left(-\frac{E_o}{RT}\right) \tag{2}$$

$$k_r = k_{or} \exp\left(-\frac{E_r}{RT}\right) \tag{3}$$

where k_{oo} and k_{or} are the pre-exponential factors and E_o and E_r are the activation energies for the two considered reactions.

The values of these parameters calculated for the three compounds studied in this work are shown in Table 3. The values of the correlation coefficient (r^2) were higher than 0.995 in all the cases, with 20 experimental points for each compound. Kinetic results are also summarised in Fig. 7. It can be observed that the fit is good, especially in the case of hexane and benzene.

The values of the model parameters indicate the different behaviour of the aromatics and hexane. So, the values of k_i are very similar for the two aromatic compounds, whereas for hexane, the value of the pre-exponential factor is 3 orders of magnitude higher than for the aromatics, and the activation energy is also higher.

Regarding to the value of k_o it is important to remark that, according to the postulates of the model, this parameter should be independent of the hydrocarbon that is oxidized. In our case, this is approximately true for benzene and toluene, but the calculated value of k_o for *n*-hexane is very different. Similar behaviour was observed for oxidation of organic compounds by other authors, Gangwal et al. [16] for *n*-hexane, and Dangi and Abraham [23] for *methyl-tert-butyl* ether.

Table 3
Kinetic constants for the oxidation of benzene, toluene and hexane (single compounds)

Compound	k_{oo} (mol seg^{-1} g^{-1} Pa^{-1})	E_o (kJ/mol)	k_{or} (mol seg^{-1} g^{-1} Pa^{-1})	E_r (kJ/mol)	r^2
Benzene	130.75	97.4	1.77×10^5	101	0.995
Toluene	33.07	99.6	1.34×10^4	106	0.995
Hexane	1.12×10^7	126	6.3×10^8	133	0.995

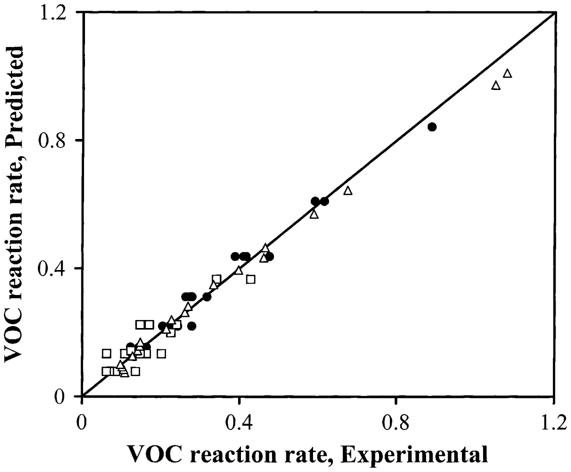


Fig. 7. Parity plot comparing the experimentally measured conversion of benzene (●); toluene (□); hexane (△) when are fed individually with the prediction of the basic Mars–Van Krevelen model (Eq. (1)).

Some authors suggested the presence of different reduction states of the metal in the catalyst, depending on the oxidised hydrocarbon [16,23]. However, Gland et al. [31] showed that all the oxygen atoms in the Pt crystal are equivalent at these temperatures, appearing different oxidised sites only at temperatures higher than 525 °C.

3.5. Kinetic modelling: binary mixtures

Assuming Mars–Van Krevelen mechanisms, the inhibition phenomena observed in the oxidation of binary mixtures of hydrocarbons could be explained according to two different models.

The first one (so-called competitive model) explains the inhibition by competition between the hydrocarbons for adsorption on the catalyst. The model considers that the chemisorbed oxygen reacts with adsorbed hydrocarbon, instead of with hydrocarbon from the gas phase. Furthermore, oxygen and the hydrocarbons are adsorbed on different sites. So, for each hydrocarbon, Eq. (1) is transformed to:

$$(-r_{\mathrm{r}})_i = \frac{k_{\mathrm{o}} k_{\mathrm{ri}} \theta_{\mathrm{i}} p_{\mathrm{O}_2}}{k_{\mathrm{o}} p_{\mathrm{O}_2} + \nu k_{\mathrm{ri}} \theta_{\mathrm{i}}} \qquad (4)$$

where θ_{r} is the surface coverage of the considered hydrocarbon. For strong interaction between the hydrocarbon and the surface, the fraction surface coverage of hydrocarbon 1 in a binary mixture of hydrocarbons 1 and 2 is given by $\theta_1 = b_1 p_1/(b_1 p_1 + b_2 p_2)$, where b_i and p_i are the adsorption constant and partial pressure of the ith hydrocarbon, respectively. The rate equation for hydrocarbon 1 in the binary mixture is then:

$$(-r)_{1/(1+2)} = \frac{k_{\mathrm{o}} k_1 p_{\mathrm{O}_2}}{k_{\mathrm{o}} p_{\mathrm{O}_2}[1 + (b_2 p_2/b_1 p_1)] + \nu_1 k_1 + \nu_2 k_2 (b_2 p_2/b_1 p_1)} \qquad (5)$$

The adsorption parameters b_i, are usually assumed to present a Van't Hoff dependence on temperature. However, considering that the ratio of the adsorption constants for 1 and 2 always appears in the model, it is reasonable to consider this ratio as a constant [17] in order to avoid an excess of parameters in the fit. This model with the mentioned assumptions was successfully used by Barressi and Baldi for mixtures of benzene, toluene, xylene and ethenylbenzene, and for ethanol in the presence of aromatic compounds [17,28].

The second model, called non-competitive, considers a reaction mechanism very similar to the original Mars–Van Krevelen mechanism, i.e. reaction between gas phase hydrocarbons and oxidised sites of the catalyst. In addition, it considers that each hydrocarbon reduces the catalytic species to a different oxidation state. So, for the oxidation of a binary mixture, the following elementary steps may be postulated:

$$\text{Cat-O} + R_1 \xrightarrow{k_1} \text{Cat-1} + \text{products}$$

$$2\text{Cat-1} + \nu_1 \mathrm{O}_2 \xrightarrow{k_{\mathrm{o}_1}} 2\text{Cat-O}$$

$$\text{Cat-O} + R_2 \xrightarrow{k_2} \text{Cat-2} + \text{products}$$

$$2\text{Cat-2} + \nu_2 \mathrm{O}_2 \xrightarrow{k_{\mathrm{o}_2}} 2\text{Cat-O}$$

Assuming the steady-state approximation and in conjunction with an overall site balance, the following reaction rate equation can be obtained:

$$(-r)_{1/(1+2)} = \frac{k_{\mathrm{o}_1} k_1 p_{\mathrm{O}_2} p_1}{k_{\mathrm{o}_1} p_{\mathrm{O}_2} + \nu_1 k_1 p_1 + \nu_2 (k_{\mathrm{o}_1}/k_{\mathrm{o}}) k_2 p_2} \qquad (6)$$

This model was used by Dangi and Abraham [23] for benzene-*tert* butyl ether mixtures and by Gangwal et al. [16] for benzene–hexane mixtures.

Table 4
Kinetic constants for the oxidation of binary mixtures according to the competitive model (Eq. (5))

Mixture	k_o (mol s^{-1} g^{-1} Pa^{-1})	E_o (kJ/mol)	k_{o_1}(mol seg^{-1} g^{-1})	E_{a_1} (kJ/mol)	k_{o_2} (mol s^{-1} g^{-1})	E_{a_2} (kJ/mol)	b_1/b_2	r^2
Benzene (1) –toluene (2)	3.39×10^6	97.4	7.34×10^8	121	1.60×10^7	112	0.14	0.990
Benzene (1) –hexane (2)	4.50×10^6	98.4	2.15×10^{10}	128	1.41×10^8	116	5.17	0.985
Toluene (1) –hexane (2)	3.40×10^6	97.4	1.56×10^{10}	125	4.50×10^6	109	65.4	0.985

Table 5
Kinetic constants for the oxidation of binary mixtures according to the non-competitive model (Eq. (6))

Mixture	k_{oo_1}	E_{o_1}	k_{oo_2}	E_{o_2}	k_{o_1}	E_1	k_{o_2}	E_2	r^2
Benzene (1) –toluene (2)	1.47×10^9	97.4	1.24×10^{11}	112	1.37×10^3	97.4	1.382×10^2	90.6	0.995
Benzene (1) –hexane (2)	7.74×10^9	95.1	8.59×10^{14}	134	2.05×10^{11}	121	1.852×10^2	88.5	0.975
Hexane (1) –toluene (2)	6.49×10^{13}	140	9.60×10^{11}	108	2.37×10^4	100	5.714×10^6	116	0.965

See units in Table 3.

The values of the parameters obtained by fit both models to the experimental results are shown in Table 4 (competitive model) and Table 5 (non-competitive model).

If only statistical criteria are considered, both models give a fairly good fit, being slightly better the fit for the competitive model. From a mechanistic point of view, the numerical results of the competitive model make more sense. So, for the competitive model the calculated kinetic constants for oxygen chemisorption (k_o) are very similar for the three mixtures studied, as predicted by the model. The calculated kinetic constants for the compounds studied (benzene, toluene or hexane), are also similar for the different mixtures, in accordance to the proposed model (they are intrinsic parameters, independent of the other compounds present in the mixture). Concerning to the adsorption constants, although it is not possible to obtain numerical values, the relative values can be compared. In the case of the toluene–benzene mixture, the ratio between the corresponding adsorption constants indicates that the strength of adsorption of toluene is higher than for benzene. As discussed previously, this behaviour can be explained by the inductive effect of the methyl group on the aromatic structure, that favours the adsorption of toluene. A similar value of the adsorption constant ratio was calculated by Barresi and Baldi [17]. Concerning to the benzene–hexane and toluene–hexane mixtures, it can be observed that the strength of adsorption of hexane is lower than that for benzene and specially for toluene, as expected, considering that the aromatic structure favours the adsorption of these compounds. This result agrees with the observed lack of inhibitory effect of hexane.

The goodness of the fit for the competitive model, especially for toluene, for all the experimental results, can be observed in Fig. 8 (benzene), Fig. 9 (toluene) and Fig. 10 (hexane).

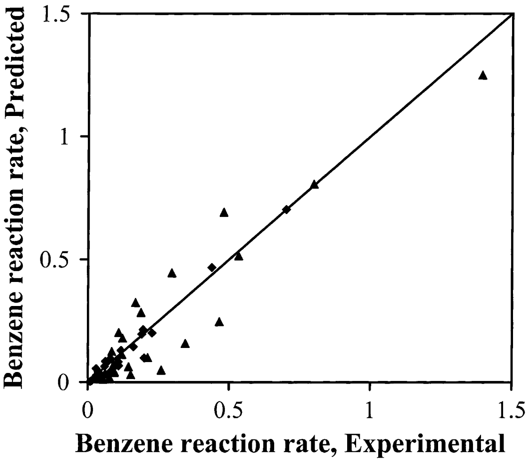


Fig. 8. Parity plot comparing the experimentally measured conversion of benzene with the prediction of the competitive Mars–Van Krevelen model (Eq. (5)) in the oxidation of benzene–toluene mixtures (◆) and in hexane–benzene mixtures (☐).

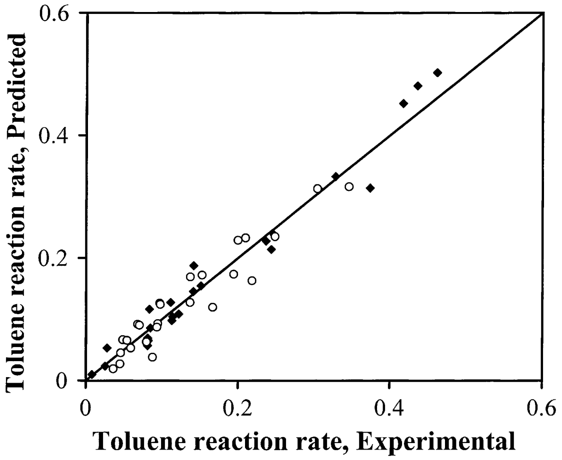


Fig. 9. Parity plot comparing the experimentally measured conversion of toluene with the prediction of the competitive Mars–Van Krevelen model (Eq. (5)) in the oxidation of benzene–toluene mixtures (◆) and in hexane–toluene mixtures (○).

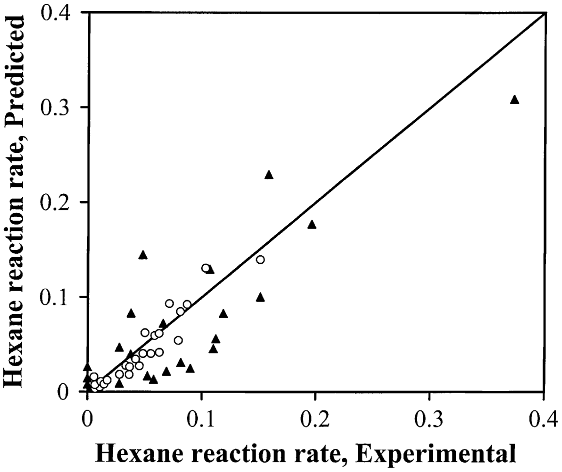


Fig. 10. Parity plot comparing the experimentally measured conversion of hexane with the prediction of the competitive Mars–Van Krevelen model (Eq. (5)) in the oxidation of hexane–benzene mixtures (□) and in hexane–toluene mixtures (○).

Acknowledgements

This work has been supported by the Spanish Inter-ministerial Commission for Science and Technology under Grant CC-96-QUI-1140. The catalyst was kindly supplied by Engelhard Industries.

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