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Combustion kinetics of cyclooctane and its binary mixture with *o*-xylene over a Pt/ γ -alumina catalyst

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ABSTRACT

Combustion kinetics of the cyclooctane and *o*-xylene, alone and in their binary mixture, have been experimentally investigated over a commercial Pt/ γ -alumina catalyst. The studies were carried out in a laboratory set-up, with diluted hydrocarbon-air mixtures, typical for depollution applications. The experiments were conducted at atmospheric pressure and temperatures between 140 and 400 °C, hydrocarbons concentration 200–1000 ppmv and WHSW (mass flow rate to catalyst weight ratios) in the range 280–590 h⁻¹. The results evidenced an important inhibition of cyclooctane combustion by the presence of *o*-xylene, throughout the working domain. Based on the experimental measurements and postulating surface mechanisms, rate expressions were developed for the combustion of the two hydrocarbons, in pure state and as binary mixtures. The cyclooctane was found to react by an Eley–Rideal type mechanism, whereas the *o*-xylene combustion was explained by a Langmuir–Hinshelwood scheme.

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1. Introduction

Catalytic combustion is a subject of interest in chemical engineering, having as main applications the power generation and the abatement of the harmful volatile organic compounds (VOC) from gaseous effluents.

Referring to the second category of applications, an important class of VOC's is that of medium volatility hydrocarbons, used alone or in mixtures, as liquid fuels or solvents (*n*-hexane, xylene, white spirit etc.). Significant amounts of xylene isomers are emitted in the exhaust gases of paint factories, production of semiconductors and production and/or transport of liquid fuels. At the same time, along with saturated and unsaturated, acyclic or cyclic hydrocarbons, the xylene isomers are components of white-spirit, largely used as extraction, cleaning and degreasing solvent, in aerosol, varnish, paint and asphalt products.

There are several techniques currently used to remove the VOC from gaseous effluents, depending of the pollutant nature and its concentration. When the VOC concentration is low, there is usually used the non-recuperative method of deep oxidation (combustion). This can be conducted homogeneously (thermal combustion) or in presence of solid catalysts (catalytic combustion). The catalytic combustion ensures the achievement of total oxidation (combustion) of organic compounds to relatively harmless products (mainly CO₂ and H₂O), operating at significantly lower temperatures than thermal combustion (usually on temperature domains where the nitrogen oxidation is negligible).

Among the catalysts utilizable for VOC's combustion, the most important are the supported noble metals, some supported transition non-noble metals and their oxides (Abbasi et al., 2011; Aguero et al., 2013; Asgari et al., 2012; Rusu and Dumitriu, 2003; Urdă et al., 2013). Particularly cerium oxide

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(Varma et al., 2007; Wang and Lin, 2004) and the perovskite-type compounds such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ or LaCoO_3 were found to be highly effective for hydrocarbon combustion (Huang et al., 2008a, b). Till now, even being more expensive, the noble metal catalysts are the most used in commercially applications, due to their high activity and resistance to deactivation. Particularly, the supported Pt is the most frequently used as combustion catalyst, due to its high activity in most of the VOC combustion reactions (Liotta, 2010; Pérez-Cadenas et al., 2006). γ -Alumina is the metal support preferently used in the preparation of commercial catalysts. Nevertheless, its main shortcoming is an important sensitivity to water, one of the combustion products (Liotta, 2010).

Data regarding the relative reactivity of different classes of organic compounds in their catalytic combustion on supported Pt, Pd and Rh catalysts were published by O'Malley and Hodnett (1999), Liotta (2010) and Diehl et al. (2010). As a rule, it was observed that the reactivity decreased in the order alcohols > aromatics > ketones > carboxylic acids > alkanes. In the class of hydrocarbons there were also identified several rules regarding the reactivity in the catalytic combustion over noble metals, systematized by Diehl et al. (2010).

In the effort to develop sound kinetic models for the VOC's combustion processes, an important number of published works hypothesized different conceptual models describing their surface mechanism.

For the saturated hydrocarbons combustion over noble metal catalysts, one of proposed schemes posits that the first and the slowest step of surface reaction mechanism is a C–H bond cleavage. So, the overall molecule reactivity is depending on the average strength of all its C–H bonds, with a major role of the weakest one. This hypothesis is supported by the correlations evidenced between the reactivity of a compound and the strength of the C–H bonds in its structure (Diehl et al., 2010; O'Malley and Hodnett, 1999). Bonnemay et al. (1969) also indicate the C–H bond dissociation, as a first step during the adsorption of inferior alkanes and alkenes on platinum electrodes surface. The authors emphasized also that the carbon radical resulting from this process is deposited on a number of sites equaling the number of carbons that it contains.

Garetto and Apesteguía (2000) studied the catalytic combustion of cyclopentane on Pt/alumina catalyst. Cyclopentane oxidation was reported to follow a surface redox mechanism, with the dissociative adsorption of oxygen on platinum as the rate determining step. The results evidenced that the combustion reaction is faster on Pt particles larger than a critical value, below which the combustion rate decreases with the decrease of Pt particle size. Similar results have been reported by Grbic et al. (2004) and Padilla-Serrano et al. (2005) for the xylene isomers oxidation. Other studies are postulating that the saturated hydrocarbons combustion over Pt is following an Eley–Rideal scheme, consisting in a dissociative adsorption of hydrocarbon on adsorbed oxygen sites (Dryakhlov et al., 1982, 1983; Kiperman, 1991). This hypothesis is sustained by the observations evidencing that, at combustion conditions, the platinum surface is almost completely covered with oxygen (Gland et al., 1980; Kiperman, 1991 and references therein).

For olefins oxidation, a rupture of the C–H allylic bond is assumed to occur on active sites, leading to adsorbed allylic π -complexes, oriented in parallel with the metal surface. The next probable step is the transformation of this π -coordinated alkene–Pt species into a di- σ species, which leads to C–C bond scission and reaction with adsorbed oxygen (Diehl et al., 2010;

Golodets, 1983). For the alkyl-aromatic hydrocarbons combustion, Golodets (1983) is suggesting a mechanism where, in the rate controlling step, the C–H bonds of side groups reacts like olefins; thus, the benzyl complex ($\text{C}_6\text{H}_5\text{CH}_2^*$) is formed from toluene, similar to an allylic one. Dryakhlov et al. (1983) and Kiperman (1991) proposed a different mechanism for aromatic hydrocarbons combustion, assuming as first step the formation of a weakly bound surface complex (A-Oads) by the interaction of non-adsorbed hydrocarbon molecule (A) with adsorbed oxygen. Next, the surface complex “A-Oads” becomes saturated with oxygen and undergoes further reactions with oxygen, either heterogeneously or homogeneously. The authors are emphasizing that the hydrocarbon combustion mechanism may vary with the reaction conditions, and participation of gaseous oxygen is preferential at low temperatures, with a much greater role for the surface oxygen at high temperatures. Therefore, the involvement of the reduced and oxidized parts of the platinum catalyst surface, in the combustion mechanism, is strongly dependent on temperature.

Other studies suggest still different mechanisms. Barresi and Baldi (1992), investigating the combustion of benzene and styrene on Pt/alumina, alone and in mixtures, proposed Downie type (modified Mars–van Krevelen) mechanism, involving as rate controlling steps the surface reaction of non-adsorbed benzene with non-equilibrium adsorbed oxygen and non-equilibrium adsorbed styrene with non-adsorbed oxygen respectively. Ordóñez et al. (2002) suggested an analogous mechanism for the combustion of benzene, toluene and *n*-hexane (alone or in binary mixtures) over Pt/alumina catalyst. This was supposing that the controlling step for oxidation of all three hydrocarbons is the reaction between equilibrium adsorbed hydrocarbons and non-equilibrium adsorbed oxygen. Similarly, Gangwal et al. (1988) described the combustion of *n*-hexane–benzene mixture over Pt Ni/alumina by a mechanism assuming as rate determining step the surface reaction between non-equilibrium adsorbed oxygen and non-adsorbed hydrocarbon molecules.

A large category of published studies were focused on the reciprocal influence of components during the catalytic combustion of mixtures. Experimental studies showed that a compound might behave quite differently when oxidized in a mixture as compared with its pure state oxidation. For example, *n*-hexane oxidation over Pt catalyst was inhibited in mixture with benzene (Gangwal et al., 1988), whereas benzene oxidation over the same metal was inhibited in mixture with styrene (Barresi and Baldi, 1992). Dryakhlov et al. (1982) investigated the combustion of cyclohexane in presence of *n*-pentane and *p*-xylene. The main conclusions of this study are the following: (i) *n*-Pentane had essentially no effect on the rate of reaction of cyclohexane and *p*-xylene respectively, regardless of temperature and concentration. (ii) At maximum concentration (83.5 mmol/m^3), cyclohexane markedly inhibited the oxidation of *p*-xylene at minimal concentration of the latter (1.05 mmol/m^3). (iii) The inhibiting effect of cyclohexane diminished as the concentration of *p*-xylene was increased, disappearing almost completely at *p*-xylene concentrations over 37 mmol/m^3 . (iv) Since *p*-xylene was more strongly adsorbed than either *n*-pentane or cyclohexane, the rates of oxidation of pentane and cyclohexane were markedly diminished by the presence of *p*-xylene in the reaction mixture. The authors proposed a combustion mechanism starting with a slow dissociative adsorption of cyclohexane, hydrogen detachment on the oxygen-covered catalyst surface and

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