AN EXPERIMENTAL STUDY OF m-XYLENE COMBUSTION OVER A COMMERCIAL Pt/ALUMINA CATALYST

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m-xylene catalytic combustion was investigated in a laboratory set-up, over a commercial Pt/Alumina catalyst, using concentrations typical for depollution applications. The operating conditions consisted in temperatures within the interval 120-360 ^oC, hydrocarbon concentration in the range of 450-1300 ppmv and WHSW (volume flow rate to catalyst weight ratio) between 0.067 and 0.2 $m^3kg^{-1} s^{-1}$. In these conditions was observed a negative reaction order in respect with the m-xylene, a total m-xylene combustion being obtained at temperatures above 250 ^oC. A power law kinetic model was found to adequately correlate the   experimental data.

Keywords: m-xylene, catalytic combustion, power-law, kinetic model

1. Introduction

The xylene isomers are considered as volatile organic compounds (VOC) regularly emitted in the exhaust gases of paint factories, production of semiconductors and production and/or transport of liquid fuels.

The removal of VOC from gaseous effluents is dependent on the pollutant nature, its concentration and amount of gas effluent. One of the most recommended methods for VOC's removal is the catalytic combustion. It has the advantages of relatively low working temperatures limiting the risk of NO_x formation and the transformation of the organic compounds into less harmful total oxidation products (CO_2 and water in the case of hydrocarbons).

Among the materials featuring catalytic activity for VOC's combustion, the most important are the supported noble metals [1], some transition non-noble metals and transition metal oxides, individually or in mixtures [2]. Even being more expensive, till present the noble metal based catalysts are widely used commercially, as result of their high specific activity and their resistance to deactivation. A review of non-halogenated VOC combustion techniques on

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supported Pt, Pd and Rh catalysts was recently published by Liotta [1]. Pt is the noble metal most frequently used as combustion catalyst because of its higher activity in most of the VOC combustion reactions [1, 3].

Till present, γ-alumina is the noble metal support prevalently used in commercial applications. Nevertheless, its main shortcoming is an important sensitivity to water, one of the combustion products. Therefore, less hydrophilic materials were tested as supports for the combustion catalysts. Pérez-Cadenas et al. [3-5] and Morales-Torres et al. [6] reported better performances of Pt and Pd supported on carbonaceous materials, as compared with alumina supported Pt and Pd, for the combustion of benzene, toluene and xylenes (BTX).

Garetto and Apesteguia [7], Grbic et al. [8] and Padilla-Serrano et al. [9], studied the influence of Pt dispersion on the activity of the supported Pt catalyst in xylene isomers combustion. The results demonstrated that the combustion reaction rate is faster on Pt particles larger than a critical value, decreasing upon lowering the Pt particle size. This was explained by the stronger Pt–O bonds formed on smaller Pt particles and lower energy Pt-O bonds, more adequate to chemical reaction, formed on larger Pt particles.

The objective of this work is the experimental identification of operating conditions required for the total combustion of m-xylene lean air mixtures over a commercial Pt/Alumina catalyst and to propose a kinetic model for this process. At our best knowledge there are not published data regarding this topic.

2. Experimental

a. Materials

Liquid m-xylene of analytical purity (Merck) was used in the combustion experiments. The catalyst used was 0.5 % wt. Pt/γ-alumina, produced by Engelhard (ESCAT 26).

b. Experimental set-up

The combustion experiments were carried out in a tubular quartz reactor, placed in an electrically heated oven provided with temperature control. The pressure was measured with an electronic manometer and was close to atmospheric one. The amount of catalyst in all experiments was 0.025 g Pt/γ-alumina diluted with 0.075 g of quartz beads having the same class of dimensions, in the range of 50 – 250 μm. In order to evenly distribute the hydrocarbon flow rate on cross section and to preheat the reactants, the diluted catalyst bed, having the height of approximately 5 mm, was loaded in reactor between two layers of quartz particles. Operating parameters (temperatures, flowrates) were controlled by electronic devices. The hydrocarbon concentration was achieved by bubbling an air stream through a vessel filled with liquid m-xylene, and then diluting the

resulting mixture with the necessary flow of dry air. The attenuation of concentration perturbation was achieved by introduction a buffer vessel of about 0.5 L before the reactor. The composition at the reactor outlet was measured on-line by gas chromatography, using a Varian CP-3800 GC equipped with methanizer, FID and TCD detectors. Further details regarding the experimental procedure are given by Manta et al. [10]. The experimental set-up is presented in

Fig. 1. There are studies in the literature reporting that kinetics of benzene combustion over 0.5 % Pt/Alumina catalysts with particle sizes below 500μm is not influenced by the particle diameter [11]. Given that benzene is more reactive than xylenes [12], it was admitted that our experimental results are obtained in conditions free from internal diffusion. The chromatograph calibration was performed using a calibration mixture with known compositions of CH_4, CO, CO_2 and N_2 provided by Messer. The m-xylene concentration in the reaction mixture was determined from a multi-point calibration procedure, based on m-xylene concentrations calculated at total conversions from the resulting CO_2.

Our results are presented as light-off curves (conversion-temperature evolutions), similar with the majority of catalytic combustion studies. The m-xylene conversion was calculated based on the inlet and outlet concentration measurements. A value of one for the m-xylene selectivity transformation to CO_2 was also determined from experimental measurements for all the experiments. No catalyst deactivation was evidenced during the experimental work.

3. Results and discussions

In order to stabilize the catalytic activity, the catalyst was conditioned after its first loading in the reactor for about 25 h under air flow at 400 ºC, and further for about 20 h in a steam of air with m-xylene. The possible catalytic effects of different parts present in the reactor were assessed by performing combustion experiments in the absence of the catalyst. No noticeable effect of the reactor internals on the combustion results were found on the working domain.

The reproducibility of the experimental light-off curves was assessed by performing several experiments in similar operating conditions. The data obtained for a total flowrate of 200 mL min^{-1} and hydrocarbon concentration of 1200 ppmv are given in Fig. 2. The results presented in this figure are showing a good reproductibility of the experimental results on the working domain.

Several conversion-temperature curves were recorded for different m-xylene feed concentrations. The influence of the hydrocarbon feed concentration is shown in

Fig. **3**, where a decrease of the m-xylene conversion by increasing its feed concentration can be observed (negative reaction order in respect to m-xylene).

This influence can be explained by the competitive adsorption of both hydrocarbon and oxygen molecules on the active sites of Pt catalyst.
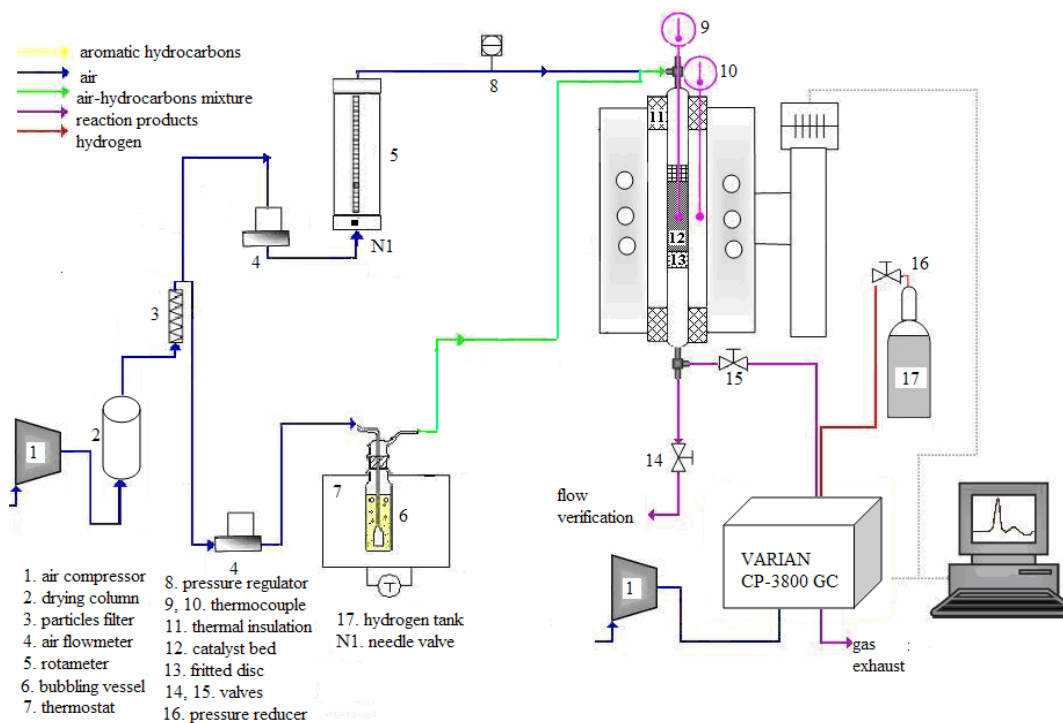

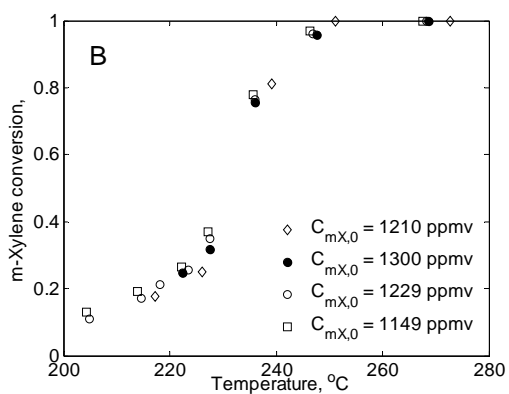Fig. 1. Experimental set-up for catalytic combustion

Fig. 2. Reproducibility of m-xylene combustion (feed flowrate of 200 mL min^{-1})

The m-xylene adsorption is enhanced by the π electrons existing in the aromatic ring. As observed from the experimental results, the hindrance effect induced by the m-xylene adsorption is amplified by increasing its concentration.
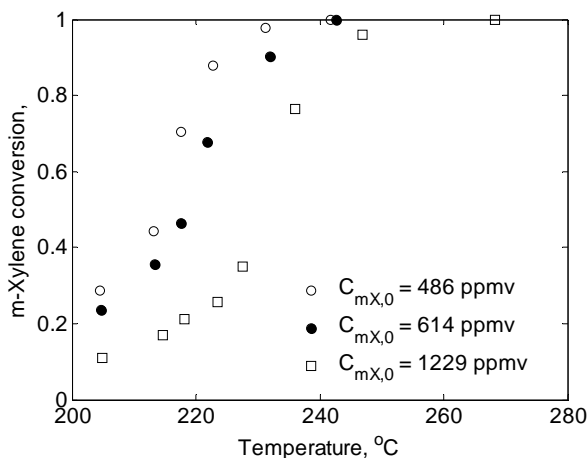

Fig. 3. The influence of m-xylene feed concentration

The π-electrons of m-xylene molecule aromatic ring are favoring its adsorption on the Pt crystallites surface. The results reported by Diehl et al. [13] and Golodets [14] are suggesting that the adsorbed m-xylene molecule on Pt consist in π-complexes, oriented in parallel with the metal surface. As in the case of olefins, the next elementary surface stage could be the reaction of these π-coordinated species to produce di-σ species, further undergoing the break of C-C bond and reacting with the adsorbed oxygen.

4. Development of a kinetic model

The stoichiometry of m-xylene combustion process is described by the overall chemical equation:

$$C_8H_{10} + \frac{21}{2}O_2 \xrightarrow{\text{cat}} 8CO_2 + 5H_2O \tag{1}$$
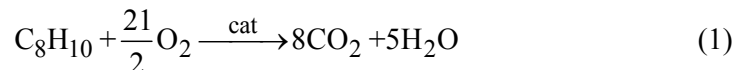
Several kinetic models are used in the literature to describe VOCs combustion over Pt/Alumina catalysts. Preliminary kinetic investigation and conceptual design studies are usually based on power law expressions. Because of the high excess of oxygen in the reaction mixture, its concentration was considered constant along the catalyst bed and equal to the one in air.

The rate expression is given by the relation:

$$r_A = k(T)p_A^n; \; k(T) = k_0 e^{-\frac{E}{RT}} \tag{2}$$

In order to diminish the correlation between the pre-exponential factor and the activation energy, the rate constant was re-written in the equivalent form [15]:

$$k = k(T_a)\exp\left(\frac{E}{R}z\right); \quad z = \frac{1}{T_a} - \frac{1}{T} \tag{3}$$

where T_a is the average working temperature, calculated as arithmetic average of the experimental values.

In this study, a pseudo-homogenous model was used to describe the process in the experimental catalytic reactor, assuming the plug flow behavior in the gas phase and considering the catalyst bed isothermal at the measured temperature (a hypothesis justified by the high degree of catalyst dilution).

The balance equation for the hydrocarbon in the gas phase is:

$$\frac{d\xi_r}{dm} = r_A; \quad m = 0, \; \xi_r = 0 \tag{4}$$

ξ_r - reaction extent; m – the mass of catalyst contacted by the reaction mixture.

The physical properties of the reaction mixture were calculated using data and relations published in the literature by Froment and Bischoff [16] and Reid et al. [17] respectively.

The kinetic parameters (k_0, E and n) were estimated using the classical least-squares method, using the "lsqcurvefit" function implemented in Matlab[®] programming environment. The error function was written in terms of relative errors in the conversion predictions:

$$J(x) = \sum_{i=1}^{N}\left(\frac{X_{e,i} - X_{c,i}}{X_{e,i}}\right)^2 \tag{5}$$

X_{ci}, X_{ei} - calculated and experimental values of m-xylene conversion corresponding to the measurement i.

In order to insure that the kinetic parameters were calculated based on experimental data free from the influence of the physical steps, m-xylene conversion values below 0.4 were used in the estimation. The estimated parameters along with their confidence intervals and the correlation coefficient are given in Table 1. The relatively close confidence intervals of parameter estimates and relatively high correlation coefficient (ro2=0.957), indicate that the proposed power law kinetic model provide a good agreement between the calculated and

experimental conversion values on the estimation interval (conversions below 0.4). As it can be observed from Table 1, a negative reaction order was determined, value in agreement with the experimental observations.

The comparison of the theoretical and experimental light-off curves presented in

Fig. **4** is evidencing a good adequacy of the proposed kinetic model predictions with the experimental results, especially for conversions up to 40 %.

The goodness of fit for the proposed kinetic model can be also revealed by the parity diagram, presented in

Fig. **5**, showing the calculated m-xylene conversion values versus the experimental ones.

The diagram presented in Fig. 5 is divided in two zones, the first one consisting in conversion values used in the estimation, and the second including values not involved in the estimation calculations.
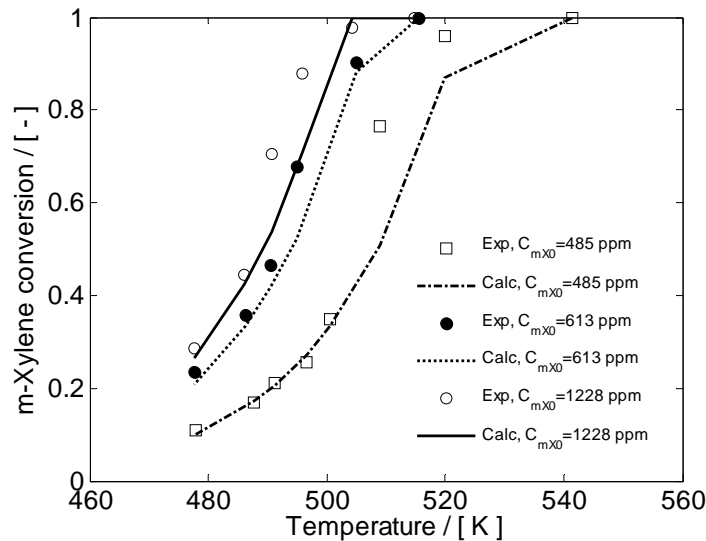

Fig. 4. Comparison of calculated and experimental light-off curves

Table 1

Kinetic parameters values and their corresponding confidence intervals

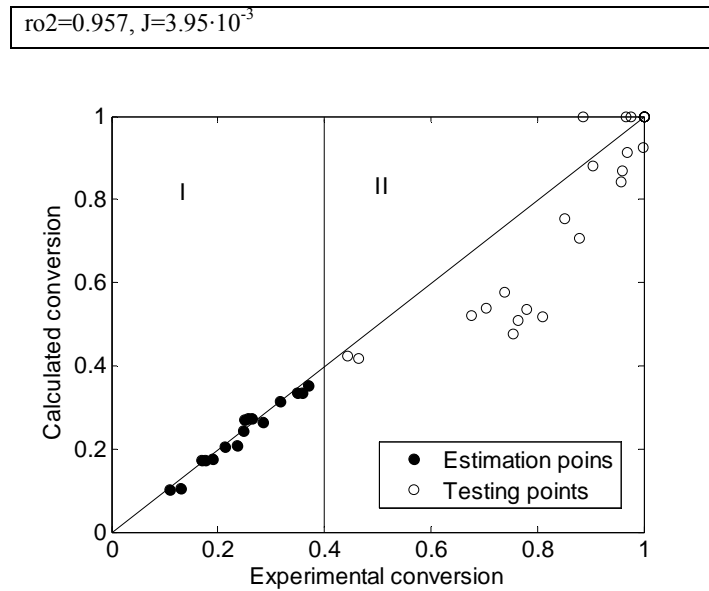| Parameter	Value	Measurement unit
k_0	$6.269 \cdot 10^{-15}(1\pm0.028)$	$kmol\ kg^{-1}\ s^{-1}\ bar^{-n}$
E	$1.251 \cdot 10^{4}(1\pm0.0043)$	$cal\ mol^{-1}$
n	$-0.05(1\pm0.102)$	-

ro2=0.957, J=3.95·10⁻³

Fig. 5. Parity diagram

The second region reveals a significant underestimation of conversion values by the reactor model considered. This can represent the effect of an axial temperature gradient arising along the catalyst bed, or significant gas to particle temperature gradients, at m-xylene conversions higher than 50 %.

5. Conclusions

The catalytic combustion of m-xylene over 0.5 % wt. Pt/Alumina commercial catalyst, particularly for VOCs removal applications, is featuring a negative reaction order with respect to hydrocarbon concentration, because of a competition with oxygen for Pt active sites. The experiments evidenced that the complete combustion of m-xylene in air at concentrations between 450 and 1300 ppmv, at space velocities between 0.067 and 0.2 m^3 kg^{-1} s^{-1} can be accomplished at temperatures above 250 ^{o}C. No significant carbon monoxide concentrations were observed in the working interval, the Pt insuring total m-xylene combustion to carbon dioxide and water. The results are useful for the analysis and design of the catalytic reactors for combustion of VOCs mixtures containing m-xylene vapour, specific for depollution applications.

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