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Pyrolysis of propane for CVI of pyrocarbon Part II. Experimental and modeling study of polyaromatic species

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Abstract

In this work, we have studied the pyrolysis of propane at high temperature and low pressure. The pyrolysis produces various hydrocarbons from light species, such as methane or hydrogen, to polyaromatic hydrocarbons species (PAH), such as benzofluoranthene ($C_{20}H_{12}$). Experimental data have been obtained in a perfectly stirred reactor and in a wide range of temperature (1173–1298 K) and residence time (0.5–4 s). During the pyrolysis, 29 species were first identified by gas chromatograph–mass spectroscopy and quantified by gas chromatography (GC).

In part I [I. Ziegler, R. Fournet, P.M. Marquaire, J. Anal. Appl. Pyrolysis, in press] of this work, a detailed kinetic mechanism (87 species involved in 386 reversible reactions) for the pyrolysis of propane was proposed, in order to reproduce the experimental gas phase species up to toluene. The validation of the mechanism was performed by simulations and comparisons with experimental data. The present work proposes an extended kinetic mechanism for the propane pyrolysis, in order to reproduce heavier species than toluene (608 reactions involving 172 species). This new mechanism allows to reproduce the formation of all the major products, identified experimentally, up to pyrene ($C_{16}H_{10}$).

Based on the simulations performed, a flow rate analysis allows us to build the major route of the formation of PAH during the propane pyrolysis. The significant roles of radicals as propargyl (C_3H_3), cyclopentadienyl (C_5H_5) and indenyl (C_9H_7) in the formation of PAH will be discussed.

Keywords: Pyrolysis; Propane; Jet stirred reactor; PAH; Pyrocarbon; Radical mechanism; Modeling; Sensitivity analysis; Flow analysis

1. Introduction

This work relates to the study of the kinetic of pyrocarbon deposition in order to produce composite carbone/carbone (C/C). Indeed, composites C/C are obtained by depositing a matrix of pyrocarbon in carbon fibers by pyrolysis of a gaseous hydrocarbon; this process is called chemical vapor infiltration (CVI). Pyrolysis is carried out at low pressure (i.e. 1–50 kPa) and high temperature (i.e. 900–1500 K). It produces, in addition to pyrocarbon, hydrogen and various hydrocarbons from light species, such as methane, to polyaromatic hydrocarbons species (PAH). The very slow kinetics of the deposit imposes high costs of production. In order to improve the kinetics of deposition, it is important to understand the reactions involved in the pyrolysis of the reactant and the mechanism of pyrocarbon deposition.

In part I of this series of papers [1], a detailed kinetic mechanism for the pyrolysis of propane has been proposed, in order to reproduce the experimental gas phase species. This mechanism, based on elementary reactions, allowed to reproduce the formation of all the major products, identified experimentally, from methane up to toluene. The validation of the mechanism was performed by simulations and comparisons with experimental data on a wide range of temperature and residence time. However, experimental analysis has shown that heavy products, such as naphthalene or acenaphtylene are in high concentration and these heavy products were not reproduced with the mechanism presented in this first paper.

In this new part, an extended kinetic mechanism for the pyrolysis of propane is proposed in order to reproduce these large aromatic species (PAH) and to improve the previous results presented in part I [1].

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2. Experimental apparatus

A detailed description of the experimental apparatus and analytical methods has been previously presented [1,2] and we just recall here the main features. The pyrolysis is carried out in a perfectly stirred reactor made in quartz. This reactor is self-stirred by gas jets and operates at steady flow, isothermal, isobar and isochoric conditions [3–5]. Its volume is 90 cm^3 and its internal area is 100 cm^2. In this work, based on propane pyrolysis only, the reactor does not contain any carbon fibers; in this case, the heterogeneous reactions can be neglected since the ratio area/volume of the empty reactor is around 1.1 cm^{-1}. This reactor allows to know the quantitative composition of the gaseous phase in the pyrolysis conditions; this last point is essential and permits to validate, quantitatively, a mechanism of propane pyrolysis.

All the experimental data presented here have been obtained under the following experimental conditions: a total pressure in the reactor of 2.7 kPa (0.35 kPa of propane diluted in nitrogen), a temperature ranging from 1173 to 1298 K and a residence time ranging from 0.5 to 4 s.

Concerning the analysis of the products of propane pyrolysis (other than pyrocarbon), the lightest products (H_2, CH_4 up to "C_4" species) are taken at the outlet of reactor and analysed on-line by two gas-chromatographs. The heavier species (starting from five carbon atoms) are condensed at the outlet of reactor in a cooled trap with liquid nitrogen during 4 hours. They are then dissolved in 5 ml of acetone to be also analysed by gas chromatography. During each propane pyrolysis, 29 products have been quantified, but more than 30 other minor species were also identified by GC–MS [2].

3. Experimental results

3.1. Influence of temperature on propane pyrolysis

Symbols of Figs. 1 and 2 display the formation of products of the propane pyrolysis according to temperature.

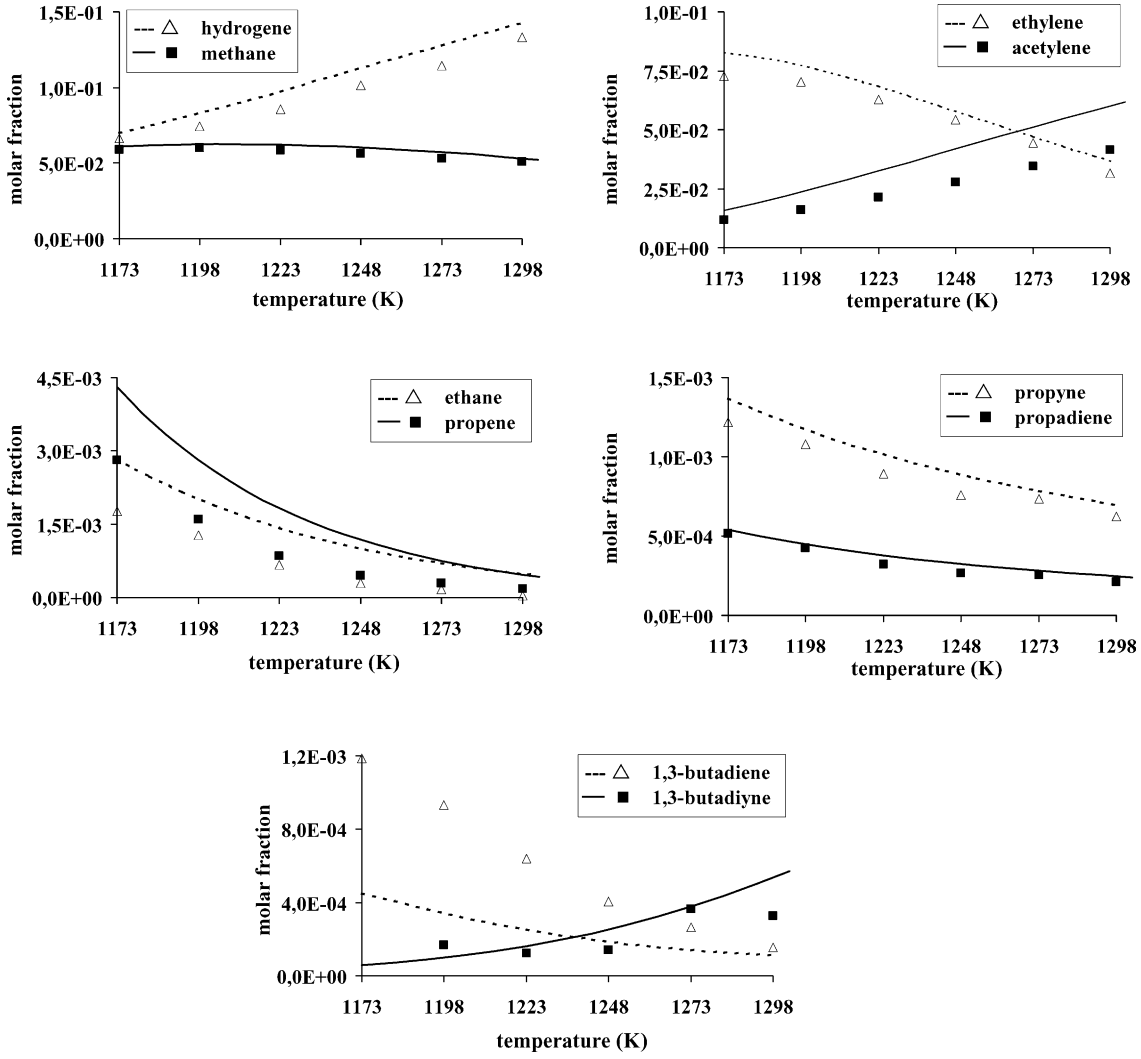

Fig. 1. Comparison between experimental (symbols) and computed (lines) molar fraction of light species vs. temperature (P = 2.7 kPa, residence time = 1 s).