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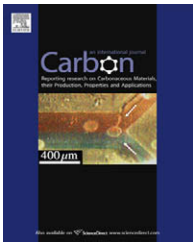

# Kinetic modeling of surface reactions involved in CVI of pyrocarbon obtained by propane pyrolysis

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ABSTRACT

A detailed heterogeneous kinetic mechanism based on elementary surface reactions has been developed to model pyrocarbon deposition obtained by propane pyrolysis on carbon fibers. The model contains 275 elementary steps involving 66 surfaces sites. It is combined with a homogeneous model in order to reproduce both deposition kinetics and gas phase composition. Deposition reactions are assumed to occur on the edges of basic structural units on both zig-zag and armchair sites. The kinetic parameters of surface reactions are estimated by analogy with a chemically similar gas phase "prototype" reaction. Simulated results are compared with experimental results obtained in a perfectly stirred reactor at low pressure (2.6 kPa) with temperature ranging from 1173 to 1323 K and residence time ranging from 0.5 to 4 s, using propane diluted in nitrogen as carbon precursor. Results show good agreement between simulations and experiments for both deposition kinetics and gas phase composition. In the chosen conditions, pyrocarbon precursors are mostly small unsaturated species (acetylene and ethylene) and methyl radicals.

## 1. Introduction

The deposition of pyrolytic carbon on solid substrates has been a subject of interest for many decades. In the petrochemical and chemical industries, carbon deposition is generally caused by highly undesirable side reactions. For example, progressive coke formation on the reactors walls of steam cracking units causes lower heat transfer, higher pressure drops and the necessity to carry out decoking operations at regular intervals [1]. Another example of undesirable carbon deposition is the progressive deactivation of catalyst, e.g. coke formation at the surface of Pt–Sn–K/$Al_2O_3$ catalyst used for propane dehydrogenation [2]. Costly decoking steps caused by coke deposition on the surface are required in order to recover an active substrate.

On the other hand, deposition of pyrolytic carbon in a well defined manner is required in order to produce carbon/carbon composites by a chemical vapor infiltration process. Those materials are widely used industrially thanks to their chemical and physical properties. Furthermore, they are four times lighter than steel, have a low thermal expansion, high thermal conductivity and their mechanical resistance and friction coefficient increase with temperature. They are consequently used in fields requiring light materials with good thermal behaviour such as the aeronautics and space industry (planes brakes, rocket and missiles nozzles, etc.). As they are also biocompatible, carbon/carbon composites are also used in the medical field as bone replacement [3]. They are usually manufactured by a Chemical Vapor Infiltration process (CVI) consisting of the progressive densification of a carbonaceous preform using a gaseous or liquid hydrocarbon as raw material. When a gaseous hydrocarbon is used to produce pyrocarbon, low deposition rates and mass transport limitations of pyrocarbon precursors within the pores of the substrate imply long infiltration duration and consequently high manufacturing costs

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[4]. A better understanding of homogeneous and heterogeneous reactions involved in pyrocarbon deposition might help optimizing carbon/carbon composites processes by decreasing manufacturing costs.

The aim of the present work is to propose a detailed kinetic mechanism modeling both gas phase and surface phase reactions. Gas phase reactions are now well known and have been the subject of previous studies for several pyrocarbon precursors such as propane [5–8], methane [9–11] or unsaturated hydrocarbons [12–14]. In this study, we use the gas phase mechanism of propane pyrolysis proposed by Ziegler et al. [5–6]. This mechanism is composed of 608 reversible elementary reactions involving 193 species. Both aliphatic and polyaromatic species production and consumption reactions are included in the gas phase mechanism. This model was validated for temperature ranging from 1173 to 1323 K and residence times ranging from 0.5 to 4 s at a total pressure of 2.6 kPa.

Regarding carbon deposition heterogeneous reactions, which are the subject of this publication, a few number of detailed kinetic mechanisms was proposed to model diamond, coke, soot and pyrocarbon formation from the gas phase. [1,12,15–17].

Frenklach and Wang [15] proposed a model composed of elementary gas phase and surface phase processes to model diamond deposition from methane–hydrogen, methane–argon and methane–oxygen–hydrogen by a Chemical Vapor Deposition process (CVD). Their detailed kinetic mechanism is composed of 158 irreversible gas phase reactions and 52 irreversible surface elementary steps in order to predict both deposition kinetics and gas phase composition. The kinetic parameters of surface elementary processes were estimated by a method derived from the collision theory. For each elementary surface process a gaseous “prototype reaction” is chosen, with surface and gas phase processes close to each other from a chemical point of view. For example, deposition of an acetylene molecule on a radical “sp2” carbon surface site is assumed to be similar to the gas phase addition reaction between a phenyl radical and an acetylene molecule. The authors then assumed that the reactions probabilities were identical for the surface elementary process and the gas phase prototype reaction.

A similar approach was used by Wauters and Marin [1] to model coke formation during steam cracking. The correction factor, which is the ratio of the pre-exponential factor of the surface reaction divided by the pre-exponential factor of the prototype reaction, is in the range $10^{-3}$–$10^{-2}$ using a calculation method derived from the collision theory. The reactions with the largest effect on the coke formation flow rate are hydrogen abstraction reactions, ipso reactions and the addition of gas phase light olefins, whereas addition of gas phase radicals has a minor influence.

Okkerse et al. [17] developed and validated a kinetic mechanism for the description of growth on the diamond surface in an oxy-acetylene torch reactor. The surface mechanism is comprised of 67 elementary steps involving 41 species, and contains methyl radicals and acetylene as diamond precursors. According to this work, acetylene has a minor role on diamond deposition compared to $CH_3$ radicals in the experimental conditions that were studied.

A global deposition model involving three potential pyrocarbon precursors was considered in a previous study [18]. This approach consists of considering that deposition reactions can be written as gas phase irreversible reactions within the homogeneous mechanism. For example, the deposition of pyrocarbon (C(B) = carbon bulk) from a gaseous species $C_xH_y$ can be written with the following empirical relation:

$$C_xH_y \rightarrow xC(B) + \frac{y}{2}\ H_2$$

The simulated rate of formation of the pyrocarbon obtained by propane pyrolysis was then compared with the experimental variation of the preform mass after a short infiltration duration (90 min). Deposition of acetylene, ethylene and anthracene were considered, with the following kinetic parameters:

$$\text{Acetylene deposition}: C_2H_2 \rightarrow 2C(B) + H_2 \quad A = 7.7 \times 10^{10}\,\text{s}^{-1}$$
$$E_A = 67{,}160\,\text{cal}\,\text{mol}^{-1}$$
$$\text{Ethylene deposition}: C_2H_4 \rightarrow 2C(B) + 2H_2 \quad A = 4.1 \times 10^{10}\,\text{s}^{-1}$$
$$E_A = 67{,}160\,\text{cal}\,\text{mol}^{-1}$$
$$\text{Anthracene deposition}: C_{14}H_{10} \rightarrow 14C(B) + 5H_2 \quad A = 3.5 \times 10^{10}\,\text{s}^{-1}$$
$$E_A = 45{,}900\,\text{kcal}\,\text{mol}^{-1}$$

If only the anthracene deposition was added in the gas phase mechanism, then the pyrocarbon simulated formation rate was underestimated. Moreover, the consumption of $C_{14}H_{10}$ was overestimated (simulated anthracene mole fraction dropped to zero whereas this species is present in experiments) and the influence of the presence of a porous substrate on the mole fractions of light species was not taken into account.

If only the deposition of light unsaturated species (acetylene and ethylene) were added in the gas phase mechanism, then the pyrocarbon formation rate was correctly predicted. The influence of the presence of carbon fibers in the reactor on the mole fraction of light species in the gas phase was also taken into account by this model. The main conclusion of that paper was that deposition of pyrocarbon obtained by propane pyrolysis can be explained by the deposition of light unsaturated species such as ethylene and acetylene, whereas the deposition of largest species only cannot explain the experimental pyrocarbon deposition rate.

A global deposition model is frequently used when transport phenomenon are taken into account. Vignoles et al. [19] developed a modeling approach, aimed at determining the importance of gas diffusion and deposition kinetics during deposition. The model is presented, validated and discussed. Deposition of acetylene, benzene and naphthalene is taken into account in the model.

Similar approaches were considered in pyrocarbon CVI from methane. Li et al. [20] successfully developed and validated a model composed of acetylene, ethylene and benzene deposition within a substrate made of braided carbon fibers. Original kinetic data of surface reactions was obtained by fitting simulated results with experimental results obtained in a CVD process. The three effective kinetic rates are defined as a function of $k_i$ and $f_i$ (hydrogen inhibition function).

Depending on the conditions, hydrocarbon pyrolysis leads to various nanotextural forms of pyrocarbon, from nearly isotropic to highly anisotropic (i.e. similar to graphite structure).