

MODELING STUDIES OF THE PREPARATION OF C/C COMPOSITES BY THE CVI PROCESS OF PROPANE

D. Hwang¹ and G. Chung^{2*}

* Department of Chemical Engineering, Hong-Ik University,
72-1 Sangsudong, Mapoku, Seoul, 121-791, Republic of Korea

* gychung@hongik.ac.kr

Keywords: CVI, Modeling, Propane, Pyrolysis Carbon, C/C Composites

1 INTRODUCTION

Pyrolysis of propane like that of many other hydrocarbons leads to hundreds of species and reactions [1~3]. Fig. 1 is the reaction mechanisms of the pyrolysis of propane. Firstly, methyl, ethyl, and n- & i-propyl radicals are produced. Then the gas products, such as methane, ethylene and acetylene, are generated [4,5]. Benzene and toluene are also produced. Ziegler et. al. [5-7] carried out the pyrolysis of propane in a wide range of temperature (1,173~1,298 K) with a residence time of 1 s. The pyrolysis generates various gaseous species such as hydrogen, various light hydrocarbons, aromatic and polyaromatic hydrocarbon species (PAH). Khan et. al. [8] also pyrolyzed propane in a flow reactor system at temperatures ranging from 913 to 1,283 K. The products of pyrolysis were collected and analyzed.

Ziegler et. al. [7] used 12.96% of propane in nitrogen at 2.625 torr. On the other hand, Khan et. al. [8] used 0.5% propane in nitrogen of 12.5 cc/min at 6 torr. In this research, pure, 20%, and 5% propane in nitrogen was used and effects of the propane concentration were observed.

CVI was originated in efforts to densify porous graphite bodies by infiltration of carbon [9]. In this process how the preforms are filled with deposited carbon uniformly without any remaining pores is the main concern of many researchers.

Modeling of the manufacturing of fiber-reinforced ceramic composites by CVI was studied by many researchers. Numerical simulations were used to optimize parameters of CVI processes. In the research of CVI of SiC, it was assumed that an overall deposition reaction is the first order on the reactant concentration and the surface area available for deposition [10,11]. The same assumptions were used in this research.

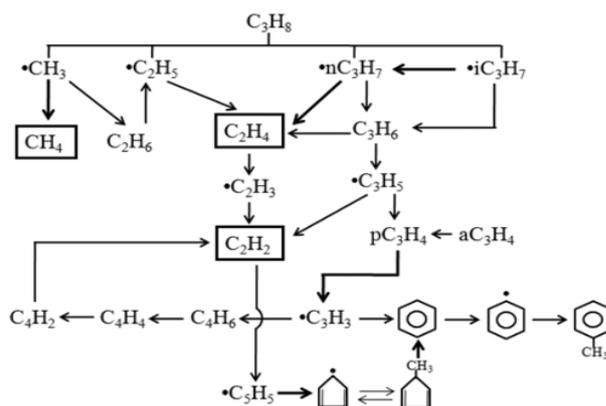


Fig. 1. Reaction mechanisms of the pyrolysis of propane at 1,248K. The products detected in this research are methane, ethylene and acetylene. The reaction paths for the production of big molecules were simplified. Details are in the references 4-6.

This work describes the experimental and modeling studies of the formation of pyrocarbon obtained by the pyrolysis of propane at 1,173~1,233 K. The amount of deposited carbon and the compositions of the exit gas after the deposition reaction were measured. The mathematical modeling of the system has been done with the deposition rate constant from the reference [12]. Time changes of the amount of deposition were estimated and compared with the experimental data. Changes of the shapes of deposited carbon in the pores of preform were confirmed with SEM photos.

2 MODEL DEVELOPMENT

Fibers in the cylindrical preform are assumed non-porous. It is also assumed that pores distributed evenly in the whole preform as shown in Fig. 2.

The reactant gas, i.e., propane, flows from one side of the preform to another in the isothermal reactor. For the gas concentration distribution, a pseudo-steady state was assumed. It is supposed that propane infiltration reaction is a first order reaction of propane by which 1 mole of propane creates 3 mole bulk carbon [13].

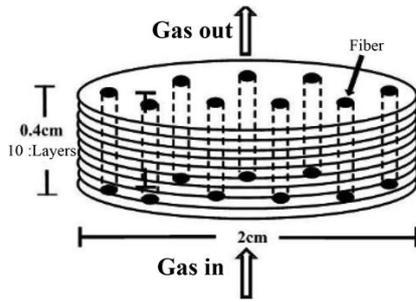


Fig. 2. Schematic diagram of the preform used in the numerical modeling.



Vaidyaraman et. al. [16] reported the rate constant for carbon deposition from propane as follows.

$$\ln k_s = 2.2 - 23,610/RT \quad (2)$$

Here, k_s [$cm \cdot s^{-1}$] is the rate constant for deposition on the surface, R the gas constant [$cal \cdot gmol^{-1} \cdot K^{-1}$], and T [K] the reaction temperature. They obtained the activation energy as $23.6 \text{ kcal} \cdot mol^{-1}$ which is much lower than the $48 \sim 60 \text{ kcal} \cdot mol^{-1}$ reported in the literature [14].

3 EXPERIMENTAL

The experimental procedures are as follows. The carbon preform was dried and weighted. This preform in the graphite tube was positioned at the center of the tube furnace. 30 cc/min of propane was injected at 30 torr as the furnace reached 1173K. 100, 20, and 5% of propane in N_2 were used. The exhaust gas was analyzed with a gas chromatograph during the reaction. The preforms after deposition were weighted and SEM photos of them were taken.

For the G.C analysis, the Porapak N packed column and TCD were used. The injection and the detection temperatures were 200 °C. The oven temperature started at 40 °C initially, and increased 20 °C/min up to 190 °C.

4 RESULTS AND DISCUSSION

4.1. Effects of Concentration

Changes of the amount of deposition with time at different concentrations are in Fig. 3. At a constant concentration, the amount of deposition increased continuously with time. The slope of a curve at a certain point is the rate of deposition at that point.

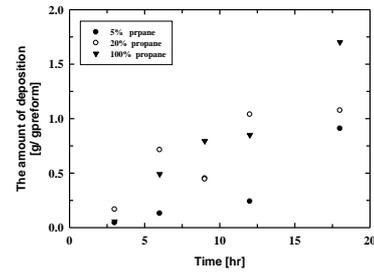


Fig. 3 Changes of the amount of deposition per unit mass of the preform as a function of deposition time at different propane concentrations

As time passed, the rate of deposition increased slightly due to the increasing surface area. This is explained in this way. The surface area is one of several driving forces for deposition. Here, the surface area is mainly the lateral surface area of fibers in the preform. Hence, the rate of deposition increases with the fiber diameters increasing due to deposition.

Fig. 4 is the initial rate of deposition per unit hour and unit mass of the preform that was obtained. When the experimental data of Ziegler et. al. [12] were multiplied by 20, their tendency was similar to ours. This means that the rate of deposition in our research was 20 times fast. This can be explained by the concentration of propane. The pure propane at 30 torr was used for our experiments. On the other hand, Ziegler et. al. have used 13% propane at 2.625 torr. The molar ratio of propane used in our experiment to that in Ziegler's experiment was almost 88. Because of this difference in the concentration, the rate of deposition had almost 20 times difference. Differences due to the other driving forces for deposition such as the initial surface area and the initial porosity of the preform could not be compared clearly because of the absence of data.

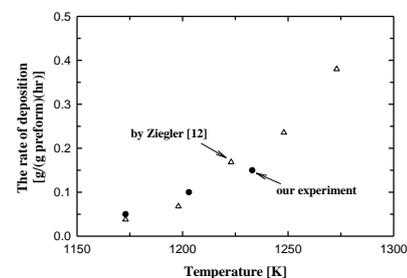


Fig. 4 Changes of the initial rate of deposition as a function of temperature.

4.2 Changes of the Shapes of Deposits

The pores are filled with the pyrolysis carbon by the CVI of propane are shown in Fig 5. It is the SEM photos of C/C composites after the deposition reactions for 9 hours. The fiber radii increased with the deposition time and the amounts of deposition on the lateral surfaces of fibers also did.

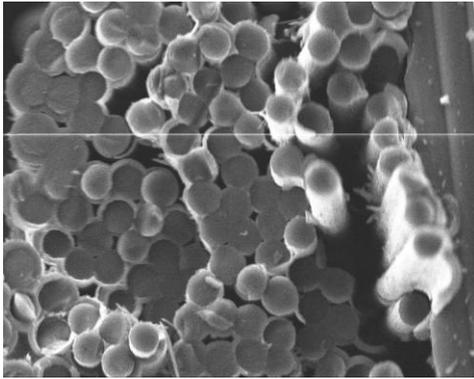


Fig. 5 SEM photograph (×1,500) of the C/C composites after the infiltration reactions for 6 hrs at 1,203 K.

4.3 Changes of the Compositions in the Exit Gas

Propane is decomposed thermally at a high temperature and produces many products. The compositions of these products at 1,173~1,278K, measured with G.C, are shown in Fig. 6(a)~(c). The methane composition slightly decreases with the reaction temperature. The ethylene composition decreases and the acetylene composition increases with the reaction temperature. The trends changing with temperature are similar with the experimental data reported by Ziegler et. al. [12]. However, the fractions of methane and acetylene were quite big and those of ethylene were small compared to the data reported by Ziegler et. al. [12].

In Fig. 6 (a)(ii)~(c)(ii), the composition changes of methane, ethylene, and acetylene at different concentrations of propane were observed at temperatures between 1,123K and 1,263K. The methane composition decreased with the reaction temperature at 5%, 20%, and 100% propane. The ethylene compositions also decreased with the reaction temperature. Concentrations of ethylene at 5% and 20% propane overlapped at temperatures between 1,163K and 1,273K. The acetylene compositions increased with the reaction temperature.

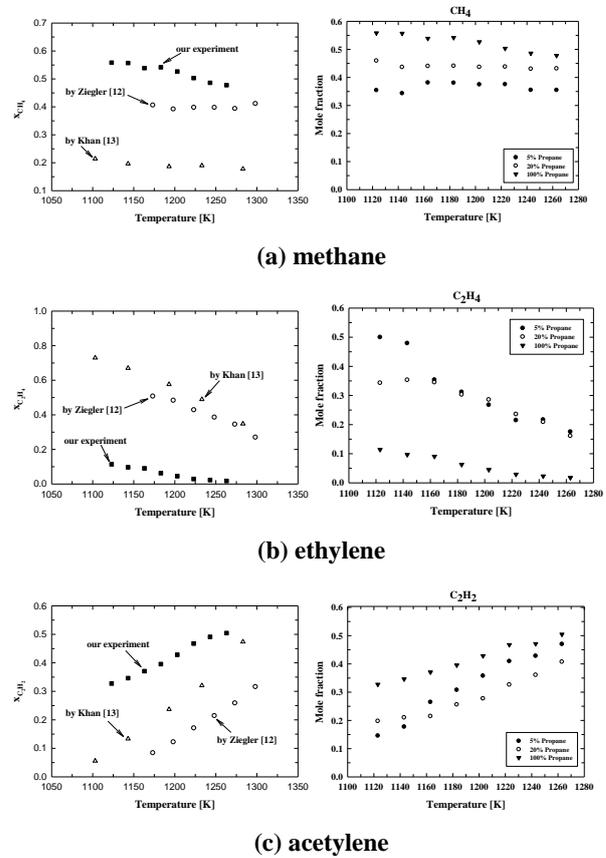


Fig. 6 Changes of the fractions of gas products with temperature at different propane concentrations : (a) methane, (b) ethylene, and (c) acetylene

4.4 The Numerical Simulation

The numerical simulations of the amount of deposition per unit mass of the preform at different temperatures and concentrations are shown in Fig. 7. Dots are experimental results and curves are modeling simulations. Results of the modeling calculations estimated the experimental data well.

The rate constant, k_s , in Eqn (2) was used for the modeling calculations. As it mentioned in the model development, Vaidyaraman et. al. [16] reported the activation energy as 23.6 kcal mol⁻¹ which is lower than 48 ~ 60 kcal mol⁻¹ reported in the literature [18]. The small activation energy reported by Vaidyaraman estimated our experimental data at 1,203 K well. On the other hand, when the rate constant was multiplied by 0.7 at 1,173 K and by 1.8 at 1,233 K, the modeling calculations fitted the

experimental data well. A smaller rate constant was used at a low temperature and a bigger rate constant was used at a high temperature.

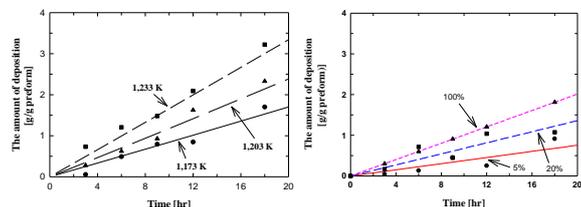


Fig. 7 Comparisons of the modeling calculations at different temperatures and propane concentrations.

5 CONCLUSIONS

In this research, the process of the preparation of C/C composites by the chemical vapor infiltration (CVI) of propane was studied. The amount of deposited carbon and the compositions of the exit gas after the deposition reaction were measured. Numerical simulations were also carried out. The following conclusions were obtained.

1. The rate of deposition increased slightly with time due to the increasing surface area.
2. At different concentrations of propane, the main gas products in the exit gas were methane, ethylene, and acetylene. The fraction of ethylene decreased and that of acetylene increased with the reaction temperature and the propane concentration. The produced propyl radicals reacted further at a high temperature and at a high propane concentration.
3. Changes of the shapes of deposited carbon in the pores of preform were confirmed with SEM photos. Most pores among fibers in the fiber bundles of the preform were filled with deposits.
4. The mathematical modeling of the system estimated the experimental data well with the deposition rate constant from the reference 16.

6 ABSTRACT

The preparation of C/C composites by the chemical vapor infiltration (CVI) of propane was studied. Effects of the concentration of propane on the infiltration were observed. Pyrolysis carbon deposited on the lateral surfaces of carbon fibers. The amount of deposited carbon and the compositions of the exit gas after the deposition reaction were estimated numerically. The rate of

deposition increased slightly with time due to the increasing surface area.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation(KOSEF) grant(NO. R01-2008-000-21103-0) funded by the Korean government.

7 REFERENCES

- [1] E.N. Wami, Chem. Eng. Technol., **17**, 195 (1994).
- [2] A.S. Tomlin, M.J. Pilling, J.H. Merkin, J. Brindley, N. Burgess and A. Gough, Ind. Eng. Chem. Res., **34**(11), 3749 (1995).
- [3] K. Norinaga and O. Deutschmann, Ind. Eng. Chem. Res., **46**(11), 3547 (2007).
- [4] C. Descamps, G.L. Vignoles, O. Féron, F. Langlais and J. Lavenac, J. Electrochem. Soc., **148**(10), C695 (2001).
- [5] I. Ziegler, R. Fournet and P.M. Marquaire, J. Anal. Appl. Pyrolysis, **73**, 212 (2005).
- [6] I. Ziegler, R. Fournet and P.M. Marquaire, J. Anal. Appl. Pyrolysis, **73**, 231 (2005).
- [7] I. Ziegler, R. Fournet and P.M. Marquaire, J. Anal. Appl. Pyrolysis, **79**, 268 (2007).
- [8] R.U. Khan, S. Bajohr, D. Buchholz, R. Reimert, H.D. Minh, K. Norinaga, V.M. Janardhanan, S. Tischera and O. Deutschmann, J. Anal. Appl. Pyrolysis, **81**, 148 (2008).
- [9] P. Delhaes, Carbon, **40**, 641 (2002).
- [10] G.Y. Chung, B.J. McCoy, J.M. Smith and D.E. Cagliostro, AIChE J., **39**(11), 1834 (1993).
- [11] M.S. Cho, J.W. Kim and G.Y. Chung, Korean J. of Chem. Eng., **13**(5), 515 (1996).
- [12] S. Vaidyaraman, W. J. Lackey, and P. K. Agrawal, Carbon, **34**(5), 609 (1996).
- [13] I. Ziegler, R. Fournet and P.M. Marquaire, J. Anal. Appl. Pyrolysis, **73**, 107 (2005).
- [14] P.A. Tesner, "Chemistry and Physics of Carbon", Edited by P.A. Thrower, vol. 9, p. 173 (1973).