

SYNTHESIS OF PYROLYTIC CARBON COMPOSITES USING ETHANOL AS PRECURSOR

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Summary

In the present paper, synthesis of pyrolytic carbon composites was investigated under chemical vapor deposition (CVD) conditions, using an oxygen-containing precursor ethanol. The influence of processing parameters such as residence time, temperature and pressure on the microstructure and the deposition rate of pyrolytic carbon was experimentally studied. A short residence time was demonstrated to favor the growth of highly ordered graphene-like pyrocarbon. Experimental results were also compared with those with methane as carbon precursor under the same CVD conditions. Much higher deposition rates but similar microstructure evolution was found out when ethanol was employed as precursor. Equilibrium calculations were performed to predict dominant gas-phase species. Furthermore, the gas-phase composition and kinetics were numerically analyzed based on a channel flow model with a detailed reaction mechanism, which explores methane is the dominated intermediate species of ethanol pyrolysis.

Keywords

1. Reaction path analysis; 2. Complex reacting flow; 3. Kinetics; 4. pyrolytic carbon.

Introduction

Chemical vapor deposition/infiltration is the mostly accepted process for the synthesis of carbon/carbon composites, in which hydrocarbons are normally employed as carbon precursors [1]. Ethanol is a bio-fuel that has been used as additive in diesel-ethanol blends in order to diminish harmful emissions in diesel engines, both gases and soot. However, the use of ethanol as an oxygenate additive to diesel fuel appears to be less desirable, since ethanol itself may contribute to particulate carbon formation [2]. Being an oxygenate, ethanol has, indeed, unusual sooting characteristics at elevated pressures, which makes ethanol an ideal candidate precursor studying CVD of pyrolytic carbon experiments. Experiments and comprehensive detailed modeling of ethanol CVD processes offer opportunities to study the fundamental behavior of an oxygen-containing precursor of carbon and the influence of an oxygenate additive to hydrocarbons on pyrolytic carbon deposition. The present work provides detailed experimental studies of the influence of CVD processing parameters on the microstructure and the deposition rate of pyrolytic carbon from ethanol as well as the first attempt to understand those experimental phenomena with a detailed kinetic model.

Experiments and Results

The pyrolysis/deposition experiments are performed with a 3k-M40 carbon fiber bundle being the substrate/preform in a $\Phi 8.4\text{mm}$ ceramic vertical flow reactor heated within a 30 cm furnace. Ethanol was vaporized into a stream of Argon. The temperature profile along the axial of the fiber bundle was measured by a k-type thermal couple. Experimental studies focus on the influence of the residence time (0.025 ~ 0.125s) and the partial pressure (1~7kPa). Polarized light microscopy was used to determine microstructures of the deposited carbon. Fig. 1 shows a scheme of the measurement approach, of which the detailed description can be found elsewhere [3].

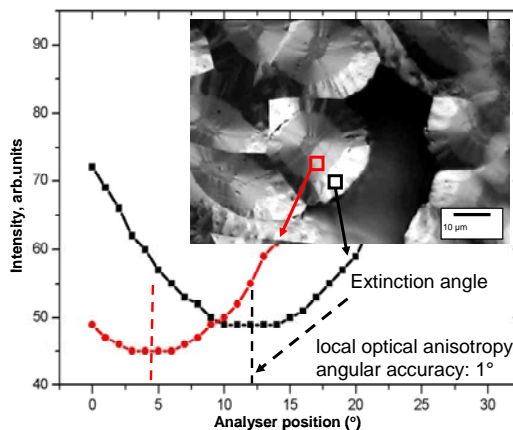


Fig. 1 Determination of the extinction angles (A_e)

i). Comparison with methane as precursor. Carbon CVD experiments with methane being pre-cursor are also carried out at the same conditions. Fig.2 clearly shows that ethanol exhibits very similar behaviours with methane working under the present CVD conditions, implying that methane is the dominant intermediate of ethanol pyrolysis.

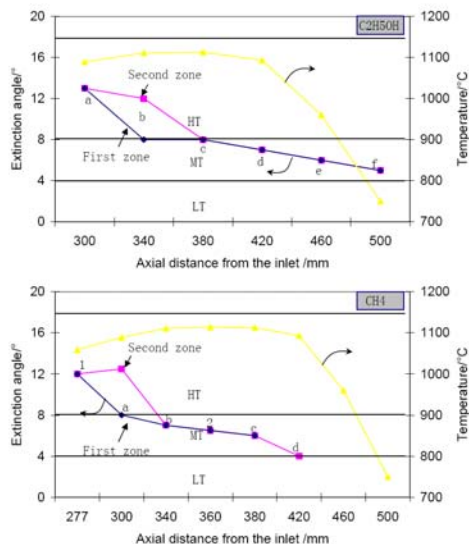


Fig.2. Comparison of textures of deposited carbon at various positions using ethanol and methane as precursor respectively (1100°C, 10h & 0.125s).

ii). Partial pressure. A partial pressure range of 1~7kPa was checked under a precondition of a fixed total pressure of 10 kPa. A lower partial pressure results in a lowly textured pyrolytic carbon. Moreover, increasing the partial pressure is beneficial to both the transition of microstructures and the deposition rate.

iii). Residence time. Experiment results with various residence times of 0.025~0.125s explore that shorter residence time will result in pyrolytic carbon with higher textures. Shortening residence time helps to suppress the transition of textures. While a lower residence time results in a higher maximum deposition rate, which may imply that deposition directly from ethanol is higher than that from those intermediates. Fig.3 shows the microstructure evolution along the axial.

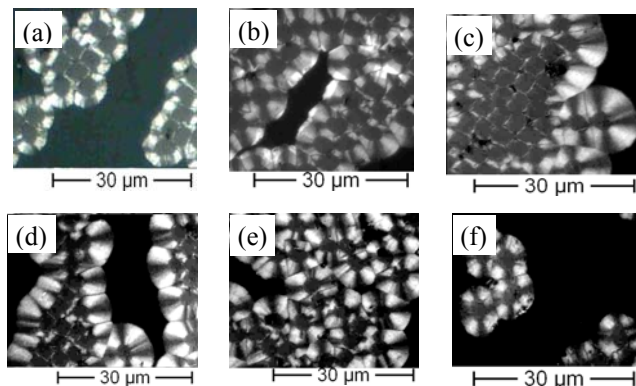


Fig.3. Corresponding polarized light microscopies along the axial, position (a), (b) (c)... are listed in Fig.2). C2H5OH, 1100°C, 10h, 5kPa & 0.125s)

More details of experimental results will be given in the full version of the paper.

Kinetic model and simulation

Since only few comprehensive studies on ethanol pyrolysis and deposition have been published, it is essential to characterize the gas-phase kinetics of ethanol and to understand how such gas-phase reactions influence the deposit formation and microstructure evolution. The detailed chemical mechanism used for the present work includes detailed pyrolysis and oxidation kinetics for hydrocarbons up to C6. It includes Marinov's ethanol oxidation mechanism, Emdee's benzene oxidation mechanism and a part of Norinaga's hydrocarbon pyrolysis mechanism [4-6]. Based on the reaction mechanism, the most important channels for ethanol dissociation are predicted through a reaction path analysis. 2D species distribution is also predicted by simulations of the complex reacting flow coupling the detailed chemical mechanism with the heat and momentum transfer model. As an example, Fig.4 shows the predicted distributions of dominant gas-phase species of ethanol pyrolysis at conditions of a temperature of 1000°C, an ethanol partial pressure of 5kPa and a residence time of 0.1s.

Equilibrium versus kinetics. We also try to predict the pyrolysis / carbon deposition at equilibrium via the minimization of total free energy approach [7]. In the equilibrium calculation of pyrolysis of ethanol, all species involved in the detailed reaction mechanism are taken into account, while graphite is also included to predict the equilibrium composition of carbon deposition from ethanol. Fig.5 shows comparison of both equilibrium calculations for those key intermediate species. Compared with the prediction of the kinetic model, equilibrium calculations demonstrate that the ethanol pyrolysis/ deposition system is far removed from equilibrium.

Details of modeling and simulations will be given in the full version of the paper

Conclusions

In the present work, experimental investigations of CVD processes from ethanol to pyrolytic carbon are carried out at various residence times (0.025 ~ 0.125s) and partial pressures (1~7kPa) of ethanol. Similar textural transition but a higher deposition rate is observed when ethanol instead of methane is used as the precursor. Shorter residence times result in pyrolytic carbon with higher textures and shortening residence time will suppress the transition of textures. Lower partial pressures result in pyrolytic carbon with a lower texture, and decreasing partial pressure will also suppress the transition of textures. It is also noticed that a short residence time results in a high deposition rate, implying that carbon deposition directly from ethanol is higher than that from those intermediate species.

A detailed reaction mechanism is used to describe the pyrolysis kinetics of ethanol. Key intermediate species are figured out through a reaction path analysis. Equilibrium calculations demonstrate that the ethanol pyrolysis/ deposition system is far removed from equilibrium..

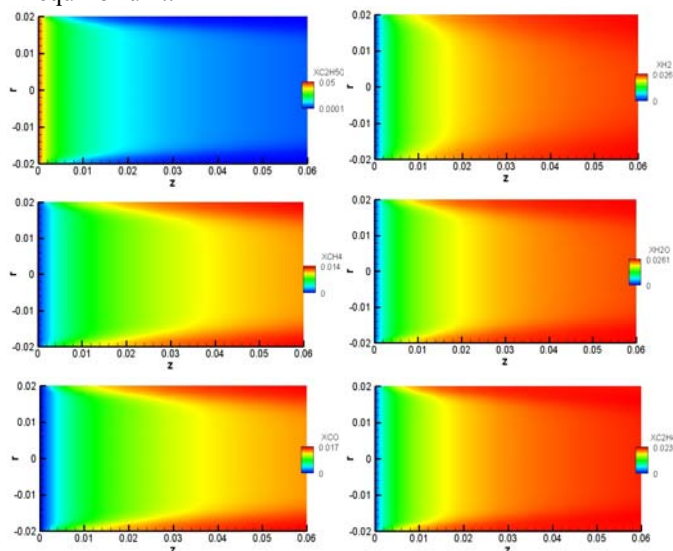


Fig.4 Predicted distributions of dominate gas-phase species of ethanol pyrolysis at conditions of a temperature of 1000°C, an ethanol partial pressure of 5kPa, a residence time of 0.1s.

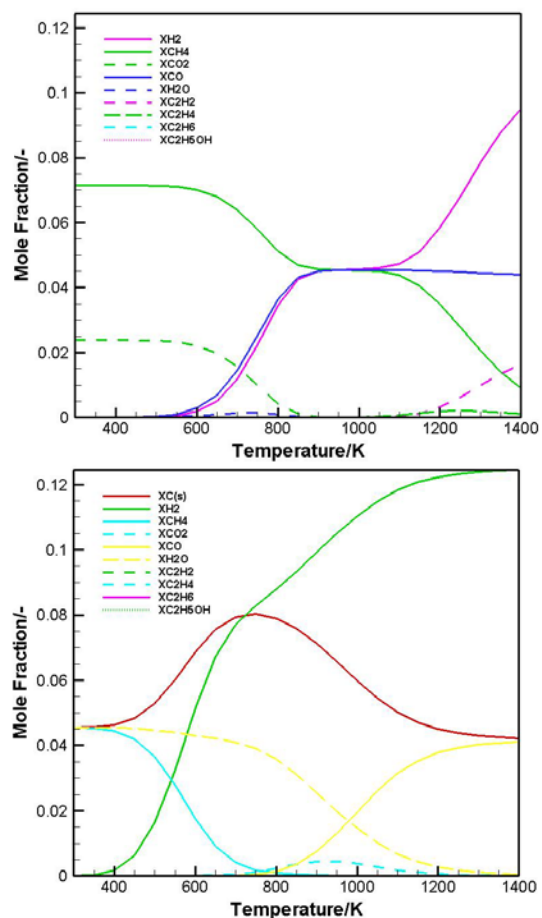


Fig.5 Equilibrium calculations of ethanol pyrolysis and carbon deposition at conditions: a partial pressure of 5 kPa with 1 total pressure of 1 atm.

References

- (1) Hüttinger KJ. Fundamentals of chemical vapor deposition in hot wall reactors. World of Carbon, Vol. 2: Fibers and Composites. Delhaes P. ed., Taylor and Francis, London, 2003: 75-85.
- (2) Li J, Kazakov A, Dryer FL. Ethanol pyrolysis experiments in a variable pressure flow reactor. Int J Chem Kinet 2001(33): 859-867.
- (3) Bortchagovsky EG, Reznik B, Gerthsen D, Pfrang A, Schimmel Th. Optical properties of pyrolytic carbon deposits deduced from measurements of the extinction angle by polarized light microscopy. Carbon 2003 (41): 2427-2451.
- (4) Marinov MN. Int. J. Chem. Kinet. A Detailed Chemical Kinetic Model for High-Temperature Ethanol Oxidation. 1999(31): 183.
- (5) Emdee JL, Brezinsky K, Glassman I. A kinetic model for the oxidation of toluene near 1200 K. J. Phys. Chem. 1992(96): 2151-2161
- (6) Norinaga K, Janardhanan VM, Deutschmann O. Detailed chemical kinetic modeling of prolysis of ethylene. acetylene and propylene at 1073-1373 K with a plug flow reactor model. Int J Chem Kinet, 2008 (40): 199-208
- (7) Deutschmann O, Tischer S, Correa C, Chatterjee D, Kleditzsch S, Janardhanan VM. DETCHEM software package, 2.1. ed., <www.detchem.com>, Karlsruhe.

