Synthesis of Pyrolytic Carbon Composites Using Ethanol As Precursor

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Chemical vapor infiltration and deposition of carbon fiber bundles are applied to synthesize pyrolytic carbon composites using the oxygen-containing precursor ethanol. The influence of the temperature (1373 and 1423 K) and pressure (1–7 Pa) on the microstructure and the deposition rate of pyrolytic carbon are experimentally studied. Higher partial pressures of ethanol are demonstrated to favor the growth of highly ordered graphene-like pyrocarbon, whereas lower partial pressures help to suppress the carbon texture transition. The gas-phase composition and reaction kinetics are numerically analyzed on the basis of a reacting flow model with a detailed reaction mechanism. Methane and C2 species are shown to be the dominant intermediate species of ethanol pyrolysis. According to the simulation, a large amount of CH3 radicals is produced, which explains the fact that the pyrolytic carbon from ethanol exhibits a texture similar to the one produced with CH4 as precursor.

Introduction

Isothermal, isobaric chemical vapor infiltration was developed in the 1960s and represents the leading manufacturing process to densify fibrous preforms with a ceramic or carbon matrix to synthesize composites, in particular, carbon/carbon composites, which are used in the aeronautic, automotive, and fuel cell industry (brakes, pistons, and electrodes).1–6 Due to the complexities of the pyrolysis of the precursor and the deposit formation, chemical vapor infiltration (CVI) from hydrocarbons into pyrolytic carbon (pyrocarbon) structures has also been of fundamental scientific interest. To reveal the essentials of CVI, most attention is paid to the impact of interactions among homogeneous gas-phase reactions, heterogeneous surface reactions, and transport phenomena on the microstructure and densification of pyrocarbon.7

Two general mechanisms have been proposed for carbon deposition from hydrocarbons: the growth mechanism and the nucleation mechanism.8–10 In the growth mechanism, carbon can be deposited as a result of light linear or aromatic species reacting on active sites at substrate edges. This process has been extensively studied with low pressure methane vapor deposition (CVD) experiments using the precursors methane, ethylene, acetylene, propane, and 1,3-butadiene.11–14 Recently, those experimental results were taken as the basis for the development of models and computational tools for the description of CVD/ CVI processes.15,16 In the nucleation mechanism, species with higher molecular weight, such as polycyclic aromatic hydrocarbons (PAHs), act as deposition precursors. This nucleation mechanism may, in particular, be realized at higher partial pressures, favoring formation of PAHs. In addition, a deficiency in active sites on the deposition surface favors this mechanism, in which the nucleation initiated by the gas phase is followed by the physical adsorption of these nuclei on the substrate surface and, finally, the deposition of carbon by dehydrogenation of these nuclei.8

The texture degree of pyrolytic carbon deposits can be analyzed by polarized light microscopy (PLM) on polished cross sections of the derived samples. The extracted increasing extinction angle, Aext, correlates with the texture degree of pyrolytic carbon deposits,17–19 and three common types of laminar pyrolytic carbon deposits can be distinguished, as shown in Figure 1: dark laminar (DL), smooth laminar (SL), and rough laminar (RL) according to the former terminology and low, medium, and high textured (LT, MT, and HT) according to the present terminology, respectively.19 The orientation of graphitic stacks in high-textured carbon is much more preferable to their orientation in low-textured carbon. Another kind of high-textured carbon deposit (i.e., a regenerative laminar (ReL) pyrolytic carbon) was described a few years ago in the densification of preforms using toluene as precursor and pressure-pulsed chemical vapor infiltration.20

Since the growth as well as the nucleation mechanisms could not be directly related to the microstructures and textures of the pyrolytic carbon, Dong and Hüttinger10 proposed a more general model, the so-called “particle-filler model”, in which aromatic hydrocarbons serve as molecular particles, and acetylene, as molecular filler. They proposed that a HT carbon is formed if the gas-phase composition exhibits an optimum ratio of aromatic to small linear hydrocarbons (acetylene); that is, an optimum particle/filler ratio.

Concerning the precursors used so far, hydrocarbons such as methane, acetylene, and propylene, often diluted by hydrogen, are widely used. To improve the density of the pyrocarbon, capillary pressure in the preform has to be increased to a certain extent. But the carbon texture transition can be suppressed by means of a technique known as pressurization. Pressurization can be realized in two ways: by pressure-pulsed chemical vapor infiltration or by isothermal, isobaric chemical vapor infiltration (ICVI).18,21 ICVI was developed to densify fibrous preforms with a ceramic or carbon matrix to synthesize composites, in particular, carbon/carbon composites, which are used in the aeronautic, automotive, and fuel cell industry (brakes, pistons, and electrodes).1

Figure 1. Schematic presentation of the preferred LT, MT, and HT orientations of pyrolytic carbon deposits. The former terminology17 is given in parentheses.
nitrogen, or argon, have primarily been used for synthesis of C/C composites.\textsuperscript{6} We think that ethanol might be an attractive alternate precursor due to potential benefits of the oxygen in the molecule.

At first thought, the presence of oxygen in ethanol rather seems to suppress carbon deposition; for instance, ethanol as oxygenate is considered a nonsooting fuel when burned at ambient conditions.\textsuperscript{21} However, at second thought, the presence of the hydroxyl group in ethanol weakens the C–H bond, suggesting increased reactivity of ethanol as compared with C\textsubscript{2} hydrocarbons and, therefore, maybe promotion of carbon deposition. Another study also revealed that ethanol can even increase formation of particulate matter.\textsuperscript{22} In this context, it is essential to characterize the gas-phase chemistry and kinetics of the pyrolysis of ethanol to understand its impact on the formation of pyrolytic carbon. The kinetics of ethanol oxidation and pyrolysis has already been studied by several groups.\textsuperscript{23–25}

In the work presented in this paper, CVD/CVI experiments were performed to study the effect of temperature and pressure on the microstructure and the deposition rate of pyrolytic carbon from ethanol. A reaction flow analysis using detailed gas-phase chemical kinetics was conducted to identify key steps and species leading to molecular weight growth in ethanol pyrolysis. Studies on the carbon deposition from ethanol will also help in the understanding of the fundamental behavior of an oxygen-containing carbon precursor or additive on the deposition of pyrolytic carbon from light hydrocarbons.

**Experimental Methods**

Experiments were performed using an isotherm, isobaric chemical vapor deposition reactor, as shown in Figure 2. To achieve better control of gas flow and residence time, bundles of high modulus carbon fibers (Toray M40–3k) were densified within a ceramic tube holder with an inner diameter of 8.6 mm. Ethanol was vaporized into a stream of argon. The wall temperature profiles along the inner tube were measured using a k-type thermal couple and are shown in Figure 3. The residence time, \( \tau \), is determined by

\[
\tau = \frac{V_R}{V_f}
\]  

where \( V_R \) is the volume of the isothermal section of the reactor chamber (~5 cm in length), and \( V_f \) the volumetric flow rate at operating conditions. The residence time of the gas mixture of 0.125 s, and the total pressure of 10 kPa was kept constant in all experiments. After 10 h of densification, the carbon fiber bundles were removed from the reactor, and the densified parts of the bundles were cut into several small pieces along the axis of bundles to determine the texture and the mean deposition rate by measuring the thickness.

For a quantitative description of the carbon matrix, the extinction angle, \( A_e \), was determined at cross sections of each piece with PLM using an improved measurement technique.\textsuperscript{26} In the case of a completely circular fiber cross section, the measurement error is about \( \pm 1^\circ \). Since fibers are not circular in reality (discussion below), the actual error is in the range of \( \pm 1.5^\circ \). The mean deposition rate of carbon on the fiber bundle matrix was computed using the photometry software of the polarized light microscope (Leitz DM RX); the systematic error is in the range of \( \pm 1 \mu m \).
The influence of the ethanol partial pressure on the carbon microstructures is studied at an operating temperature of 1373 K (within the isothermal section of the reactor chamber; the temperature profile is given in Figure 3), a deposition time of 10 h, a residence time of 0.125 s, and a total pressure of 10 kPa; that is, the dilution by Ar was varied to keep the total pressure constant. Figure 3 shows the measured profiles of the extinction angle for pyrolytic carbon formed at initial ethanol partial pressures of 1, 3, 5, and 7 kPa. An initial ethanol partial pressure of 1 kPa leads to a relatively uniform MT carbon in the isothermal part of the reactor. With increasing partial pressure of ethanol, a texture transition from MT to HT is observed in the isothermal region. Decreasing partial pressure is evidently helpful to suppress the texture transition. The regression of carbon textures (i.e., loss in texture as HT → MT → LT), however, seems to occur in the downstream part of the reactor independent of the partial pressure applied. The reason for this regression is probably the decreasing temperature in this region.

The corresponding polarized light micrographs are shown in Figure 4 for the case of an ethanol partial pressure of 7 kPa. A texture regression does occur along the axis of the fiber bundle. Moreover, two different deposition zones (i.e., first/second zone indicated in Figure 3) are formed concentrically, and microstructures exhibit a thin but distinct texture transition at the axial positions from a to c of the bundle.

More than 40 years ago, Bokros already observed an increase in preferred orientation of deposited carbon, that is, a transition from MT to HT with increasing methane concentration and temperature. He mentioned that anisotropy and density of pyrolytic carbon increase with increasing surface area of the fluidized bed. In 1970s, Pierson and Lieberman also reported the abrupt transition from MT to HT, and they attributed this phenomenon to the variation of the ratio of C2H2 to C6H6 in the gas phase. In 1999, Benzinger and Hüttlinger studied the influence of the ratio of the surface area of the substrate with its active sites, $A_s$, to the “free” volume of the reactor, $V_R$, on carbon texture transitions based on CVI experiments using fiber felts with a low carbon fiber volume fraction. They found that the evolution of $A_s/V_R$ with progressed densification of the porous preforms modifies the ratio between homogeneous and heterogeneous reaction rates and causes a shift in deposition chemistry, leading to the texture transition from MT to HT.

Later on, Vignoles et al. developed a dynamic model based on a bimolecular heterogeneous deposition reaction step to explain the sharpness of the pyrolytic carbon nano texture transition from SL to RL in CVI processes. They found that the nonlinear cross-reaction term between the absorbed light species and the absorbed aromatic species accounts for the sudden transitions in deposited nano texture, whereas the diffusive transport of the intermediate species inside the porous preform enhances the parameter domain of this phenomenon. In the present work, kinetic calculations of gas-phase pyrolysis are performed to explain the influence of ethanol partial pressures on abrupt transition of the texture from MT to HT.

The influence of the temperature on carbon microstructure is studied by running another CVI experiment, now at a reactor temperature of 1423 K, again at a deposition time of 10 h and a residence time of 0.125 s. The ethanol partial pressure was chosen to be 5 kPa at a total pressure of 10 kPa. Figure 5 compares the carbon textures produced at 1373 and 1423 K; the micrographs were taken at the axial position corresponding to the maximum temperature in the reactor. The increasing
temperature obviously results in a limited texture transition for carbon deposited near those large voids.

Figure 6 illustrates the influence of processing parameters on the mean carbon deposition rate. The deposition rate of pyrolytic carbon increases with growing ethanol partial pressures in the isothermal section of the reactor. Concerning the growth mechanism of carbon formation, saturated adsorption has not yet been achieved in the present work. In contrast to the neglecting effect on the microstructure of pyrolytic carbon, the temperature plays a major role on the deposition rate as shown in Figure 6.

Kinetic Model and Numerical Simulation. Understanding the gas-phase composition and the kinetics of ethanol pyrolysis leading to that composition is crucial for better insight into the mechanisms of carbon deposition and the evolution of the microstructure. Furthermore, this understanding may help to interpret the results of the so far only few studies recently published on the CVI of carbon composites using ethanol.

A detailed chemical reaction mechanism for the homogeneous gas-phase chemistry is used, which consists of 261 species taking part in 1177 reversible reactions. This mechanism is based on the recently developed model by Norinaga and Deutschmann, extended by the ethanol oxidation mechanism of Marinov, and parts of the toluene oxidation mechanism of Emdee et al. This new detailed reaction mechanism has recently been evaluated by simulations of the ethanol pyrolysis experiments of Peg et al.

Using the newly extended reaction mechanism, the most important channels for ethanol initial dissociation are predicted through reaction flow analysis, as shown in Figure 7. At a low partial pressure of 1 kPa, ethylene and propylene are the key intermediate hydrocarbon species, and the \( \text{CH}_3\text{CHOH} \) radical is the most important oxygen-containing intermediate species.

Since the diffusive transport along the axial direction of the tubular reactor is negligible in comparison with convective mass transport due to the high Péclet number (15.4) of the present experimental setup, the two-dimensional (2D) spatial concentrations of gas-phase species are predicted by simulations of the reacting flow through the cylindrical reactor using the boundary layer approximation coupled with the detailed gas-phase reaction mechanism and having the axial and the radial directions as independent variables. The governing equations of the system solved are

\[
\frac{\partial (rpu)}{\partial z} + \frac{\partial (rpu)}{\partial r} = 0 \quad (2)
\]

\[
\frac{\partial (rpu^2)}{\partial z} + \frac{\partial (rpuw)}{\partial r} = -\mu \frac{\partial p}{\partial z} + \frac{\partial}{\partial r} \left( \mu \frac{\partial u}{\partial r} \right) \quad (3)
\]

\[
\frac{\partial (rpuh)}{\partial z} + \frac{\partial (rpuh)}{\partial r} = u \frac{\partial p}{\partial z} + \frac{\partial}{\partial r} \left( \mu \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial r} \left( \sum k \rho h D_k \frac{M_k}{M} \frac{\partial X_k}{\partial r} \right) \quad (5)
\]

\[
\frac{\partial (rpuY_k)}{\partial z} + \frac{\partial (rpuY_k)}{\partial r} = \frac{\partial}{\partial r} \left( rP D_k \frac{M_k}{M} \frac{\partial X_k}{\partial r} \right) + r \omega_k \quad (6)
\]

where \( z \) (m) is the axial coordinate; \( r \) (m), the radial coordinate; \( u \) (m s\(^{-1}\)), the axial component of velocity; \( v \) (m s\(^{-1}\)), the radial component of velocity (kg m\(^{-1}\) s\(^{-1}\)); \( \rho \) (Pa), pressure; \( h \) (J kg\(^{-1}\)), enthalpy; \( Y_k \), the mass fraction of species \( k \); \( X_k \), the mole fraction of species \( k \); \( D_k \) (m\(^2\) s\(^{-1}\)), the diffusion coefficient of species \( k \); \( M_k \) (kg mol\(^{-1}\)), the molar mass of species \( k \); \( M \) (kg mol\(^{-1}\)), the mean molar mass; \( \mu \) (Pa s), viscosity; \( W \) (m\(^{-1}\) K\(^{-1}\)), the thermal conductivity; \( T \) (K), temperature; \( h_k \) (J kg\(^{-1}\)), the enthalpy of species \( k \); and \( \omega_k \) (kg m\(^{-3}\) s\(^{-1}\)), the gas-phase reaction rate of species \( k \). The present work focuses on gas-phase reactions; therefore, no surface reaction mechanism is involved in the present model.

After radial discretization of the above equations into \( n \) cells with boundary coordinates, a system of first-order differential equations in terms of the \( z \) coordinate (the axial direction) is attained, which is solved by a method of lines applying the DETCHEMCHANNEL code.

Figure 8 shows the 1D axial profiles of dominant species extracted from the 2D simulation results with a residence time of 0.125 s, a total pressure 10 kPa, and an ethanol inlet partial pressure of 1 and 7 kPa, respectively. The wall temperature profile shown in Figure 3 was used as the boundary condition in the simulations. Ethanol predecomposition occurs upstream of the hot zone, and only a very small amount of ethanol remains. It is clear that C\(_2\) species are the dominant species in the gas phase. From a viewpoint of growth competition from various carbon source species, formation of MT carbon in the case of an initial ethanol partial pressure of 1 kPa is controlled.
by light species due to a relatively large \( A/V_b \) of the fiber bundle at the starting point of the isothermal part of the reactor.

Increasing the initial ethanol partial pressure by a factor of 7 from 1 kPa to 7 kPa leads to an increase of the \( \text{C}_2\text{H}_4 \) concentration by just a factor of 3 and of the \( \text{C}_2\text{H}_2 \) concentration by 50%, as shown in Figure 8, resulting in much more formation of heavier species; therefore, heavy species control the deposition chemistry in the case of an initial ethanol partial pressure of 7 kPa, leading to similar MT carbon formation in the first stage as shown in Figures 3 and 4. Progressive carbon deposition on fibers of the bundle, however, dramatically increases the \( A/V_b \) ratio and results in a modification of the deposition chemistry, as expected by the particle-filler model, which may explain the concentrically formed HT carbon around fibers in the second zone observed in Figures 3 and 4. Moreover, Figure 8 shows almost constant mole fractions of the dominant gas-phase species in the downstream part of the reactor, which implies that it is not the composition change but the decreasing temperature leading to the regression of carbon textures in this region as shown in Figure 3. These calculations also suggest that a very small residence time is necessary to avoid or suppress the predecomposition of ethanol and consequently to control the gas-phase composition.37

![Figure 8](image1.png)

Figure 8. Axial distribution of the temperature and the dominant species extracted from the 2D simulation at an ethanol partial pressure of 1 (left) and 7 kPa (right), residence time 0.125 s, total pressure 10 kPa.

![Figure 9](image2.png)

Figure 9. Numerically predicted 2D profiles of the temperature and the key radicals within the tubular reactor at an ethanol partial pressure of 1 kPa and a residence time of 0.125 s.

![Figure 10](image3.png)

Figure 10. Mole fractions at thermodynamic equilibrium computed at an ethanol partial pressure of 1 kPa and total pressure of 10 kPa. (a) Solid carbon and all gas-phase species involved in the reaction mechanism are considered; (b) only ethanol, \( \text{CO}, \text{CO}_2, \text{CH}_4, \text{C}_2\text{H}_2, \text{H}_2, \text{H}_2\text{O}, \) and \( \text{C}_6\text{H}_6 \) are considered.
The predicted 2D distributions of the temperature and the key radicals within the entire reactor are displayed in Figure 9 for the case of an ethanol partial pressure of 1 kPa. It is known that hydrogen and methyl radicals significantly determine the availability of active sites for deposition on the carbon surface due to recombination reactions. The CH₂ radicals in the gas phase of ethanol pyrolysis exhibit a relatively high mole fraction, being similar to that in methane pyrolysis. This may be the reason why CVD of carbon from ethanol shows textures similar to the one from methane.

The distribution of H radicals is almost constant in the isothermal section of the reactor in Figure 9. In Figure 3, pyrolytic carbon deposited at an ethanol partial pressure of 1 kPa exhibits an almost identical texture within the isothermal section of the reactor, which may result from this constant H radicals profile. The CH₃CHOH radicals are primarily formed in the upstream part of the reactor, and significant OH radical concentrations also exist in a small region in the upstream part of the reactor. Therefore, both should not have a strong influence on carbon deposition as compared with other dominant radicals.

An equilibrium analysis of the ethanol pyrolysis/carbon deposition system is performed using the minimization of total free energy. In a first equilibrium calculation, solid carbon and all gas-phase species of the detailed gas-phase reaction mechanism are considered in the computation. Taking solid carbon into account, CO, H₂, and C(s) are the major species at equilibrium in the high temperature range, as shown in Figure 10. From a thermodynamics point of view, the following overall reaction may dominate the process at high temperatures:

\[ \text{C}_2\text{H}_5\text{OH}(g) = \text{C}(s) + 3\text{H}_2(g) + \text{CO}(g) \Delta G_{\text{1400K}}^0 = -350.18 \text{kJ mol}^{-1} \]  (7)

In CVD, the thermodynamic equilibrium may be reached inside a porous carbon fiber perform, usually exhibiting a large surface area to volume ratio, due to the long residence time. However, in the present study, a relatively small residence time is chosen, and the tubular reactor exhibits a very small surface area to volume ratio. Neither favors a rapid establishment of the equilibrium composition. In the second calculation, we consider only the light species CO, CO₂, CH₄, C₂H₄, C₂H₂, H₂, H₂O, and C₃H₆ while neglecting solid carbon, in particular. In that case, C₂H₂, H₂, and CO are the major species at equilibrium at 1400 K, as given in Figure 10b. The overall reaction governing this state then is

\[ \text{C}_2\text{H}_5\text{OH}(g) = \text{C}_2\text{H}_4(g) + 2.5\text{H}_2(g) + 0.5\text{CO}(g) \Delta G_{\text{1400K}}^0 = -275.71 \text{kJ mol}^{-1} \]  (8)

Compared to the predictions of the kinetic model (Figure 8), both equilibrium calculations demonstrate that the ethanol pyrolysis reactor is operated far away from equilibrium.

**Conclusions**

Chemical vapor infiltration of carbon was experimentally studied using the oxygen-containing species ethanol as precursor in a tubular furnace with a long fiber bundle as preform. The influence of ethanol partial pressure (1–7 kPa) and two operating temperatures (1373 and 1423 K) on carbon deposition was analyzed. Lower partial pressures result in a low-textured pyrolytic carbon, and decreasing partial pressure helps to suppress the transition between different carbon textures. It is observed that the temperature of the reactor strongly influences the carbon deposition rate, but only slightly the evolution of the carbon texture.

A detailed reaction mechanism is implemented into two-dimensional flow field simulations to describe the pyrolysis kinetics of ethanol in the CVI reactor. The simulations reveal that C₂ species are dominant in the gas phase. Large amounts of CH₃ and H radicals are formed in the gas phase, explaining why the textures of pyrolytic carbon structures obtained with ethanol and from methane as precursors are similar; CH₃ radicals are known to be the decisive intermediates when CH₄ is used as precursor. Equilibrium calculations demonstrate that the reactor is operated far away from thermodynamic equilibrium.

**Acknowledgment**

We thank Koyo Norinaga (Kyushu University) and Steffen Tischer (Karlsruhe Institute of Technology) for many fruitful discussions on the development of the reaction mechanism and the numerical simulations. We also appreciate Günther Schoch’s and Yvonne Dedecek’s editorial assistance. A.L., S.L., and O.D. gratefully acknowledge the German Research Foundation (DFG) for financial support. B.B. and O.D. gratefully acknowledge DFG for financial support through the DFG-NSF joint grant, Material World Network: Multi-scale Study of Chemical Vapor Infiltrated C/C Composites. S.Z. gratefully acknowledges a grant of the National Natural Science Foundation of China (No.50972120).

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Received for review January 31, 2010
Revised manuscript received May 18, 2010
Accepted May 20, 2010

IE100230B