CARBON 79 (2014) 28–35

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

# Chemical vapor infiltration of activated carbon with tetramethylsilane

Christian Pflitsch [a,*], Benjamin Curdts [a], Martin Helmich [b], Christoph Pasel [b], Christian Notthoff [c], Dieter Bathen [b], Burak Atakan [a]

[a] Institute for Combustion and Gas Dynamics (IVG), Thermodynamics and CeNIDE, Faculty of Mechanical Engineering & Process Technology, University of Duisburg-Essen, Lotharstr. 1, D-47057 Duisburg, Germany

[b] Thermal Process Engineering, Faculty of Mechanical Engineering & Process Technology, University of Duisburg-Essen, Lotharstr. 1, D-47057 Duisburg, Germany

[c] Nanoparticle Process Technology and CeNIDE, Faculty of Mechanical Engineering & Process Technology, University of Duisburg-Essen, Lotharstr. 1, D-47057 Duisburg, Germany

ARTICLE INFO

*Article history:*
Received 19 March 2014
Accepted 8 July 2014
Available online 14 July 2014

ABSTRACT

Chemical vapor infiltration of activated carbon with tetramethylsilane (TMS) at 200 hPa total pressure and a gas phase concentration of 15 (mol-)% TMS in nitrogen is studied. The influence of temperature on the infiltration process is discussed in detail. Up to 873 K, the infiltration is performed in the kinetically controlled regime resulting in high loadings up to around 42 (wt.-)%. The modified materials show high values for BET-surface and pore volume indicating a sufficient adoption of the infiltrated silicon layer to the surface morphology of the carbon substrates. Low oxidation resistance of the infiltrated material and EDX measurements give rise to the assumption that the infiltrated material is silicon. At higher infiltration temperatures above 873 K, particles are formed which have the shape of cylindrical nanostructures. EDX measurements reveal that silicon carbide is produced at these temperatures.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Activated carbons are important adsorbents covering broad fields of technical applications like air and gas purification [1], gas separation [2,3], decolorization and purification of solvents [4] as well as purification of liquids [5,6]. Their main technical properties are the high porosity, the high internal surface area as well as the chemical nature of its surface groups. However, some disadvantages of activated carbons are obvious, notably the low resistance against oxidation and the frail mechanical stability. These disadvantages prevent the use of these materials e.g., in continuous fluidized bed adsorbers or in strongly oxidizing environments.

One possibility to overcome these disadvantages is to cover activated carbon with an inert material while keeping surface morphology and therefore the high surface area as far as possible unchanged. This is the basic idea for the investigation presented here. It is aimed to modify the activated carbon in such a way as to render it more capable of withstanding higher temperature levels under oxidizing conditions, while at the same time maintaining its good adsorbing qualities. In order to achieve this, which would certainly advance technical

* *Corresponding author:* Fax: +49 203 379 1594.
E-mail address: christian.pflitsch@uni-due.de (C. Pflitsch).
http://dx.doi.org/10.1016/j.carbon.2014.07.018
0008-6223/© 2014 Elsevier Ltd. All rights reserved.

applicability, the coating of activated carbon with tetramethylsilane (TMS) was investigated. The long term goal is to build up a silicon carbide or silicon oxide layer all over the surface area. The following study discusses the TMS infiltration at reduced pressure of 200 hPa with respect to different temperatures. An in-depth investigation of physical and chemical properties, such as the oxidation behavior, will be subject to forthcoming publication.

Vapor phase infiltration of activated carbons with carbon or silicon carbide (SiC) was investigated previously. Methane was used for the infiltration of pure carbon in order to turn activated carbons into molecular sieves [7]. SiC-adsorbents were derived from the vapor infiltration of activated carbon with silicon chloride [8,9]. In both cases, the initial morphology of the template was well adapted or modified by the infiltration process. However, the usage of silicon chloride is always problematic as HCl is formed, which requires additional treatment of the exhaust gas flow due to its highly corrosive nature. Therefore, tetramethylsilane (TMS) was used as a precursor here, which, to our knowledge, was not used in CVI processes earlier. It has the advantage of being free of halogens, being easy to handle and having a high vapor pressure at low temperatures. Further, it is rather cheap supporting the economic feasibility of the process.

## 2. Results and discussion

The chemical vapor infiltration process (CVI) within a hot wall reactor depends on infiltration parameters such as pressure, precursor concentration, and temperature. The pressure was chosen because of the experimental setup, since the vapor pressure of TMS is relatively high, it needs to be cooled down. The cooling unit used for the precursor has a minimum temperature of 258 K at which TMS has a vapor pressure of 160 hPa. To avoid boiling of the precursor all measurements shown here were performed at 200 hPa. At this pressure, the collision rate of the precursor molecules in the gas phase is reduced and therefore gas phase nucleation, leading to unwanted powders, is shifted towards higher temperatures while the concentration is still relatively high. This increases the experimental temperature range for infiltration, which was studied here. Temperature usually strongly influences the chemical kinetics at the surface and in the gas phase. If temperature is too low, no measurable deposition occurs and the precursor passes the reactor without any reaction. In case of temperature being too high, usually a depletion of the precursor occurs towards the rear part of the reactor, resulting in an inhomogeneous deposition along the flow direction. Also gas phase nucleation and formation of particles is often observed. The gas phase concentration of TMS was kept at a high level for a good infiltration impact, but it was also limited to the vapor pressure of the precursor within the bubbler used and to the nitrogen flow used as carrier gas. Experimental measurements, over the course of which the bubbler was weight before and after deposition, lead to a TMS concentration of 15 (mol-)%.

In principle, the chemical vapor infiltration (CVI) process is based on the thin film chemical vapor deposition (CVD) of tetramethylsilane on the inner surface of the carbons. For the CVD process reliable models exist to describe the growth mechanism in detail [10]: The mass growth rate $\dot{m}$ is dominated by an Arrhenius-term for reaction limited conditions. In case the chemical surface reaction is of first order, it can be formulated as:

$$\dot{m} \propto A \cdot C \cdot \exp\left(\frac{E_a}{R \cdot T}\right) \quad (1)$$

Here, $A$ is the surface area, $C$ is the gas phase concentration of the precursor, $E_a$ is the activation energy of the surface reaction, $T$ is the deposition temperature, and $R$ is the universal gas constant. For infiltration in porous media the theoretical description becomes more complex, because the diffusion within the pores has to be taken into account. Thereby pore size and geometry have to be known. A good example for such model was e.g., shown by Popovska et al. [11] for the infiltration of titanium carbide (TiC) into porous media. It bases on the Thiele-modulus (TM), which describes the relation between the diffusion and the kinetics of the surface reaction. In case of large values for the TM, the pores are filled homogeneously. For small values the entrances of the pores are easily blocked. However, such detailed model is difficult to develop in the present study, because activated carbon is a natural product and therefore the pore geometry is not well defined or even known. Nevertheless, the following measurements can be qualitatively discussed on the base of Eq. (1).

### 2.1. Mass changes during infiltration

In order to study the temperature dependence of the infiltration process, several measurements between 650 K and 1100 K were performed while the mass of the infiltrated activated carbons were in-situ recorded. Typical mass changes as a function of the infiltration time for three temperatures are shown in Fig. 1a (819 K, 852 K and 869 K) and Fig. 1b (1096 K).

At 869 K and below, no particle formation is observed (Fig. 1a). For 869 K and 852 K the slopes show saturation behavior while for 819 K the measurement was stopped before saturation was reached because growth rate is too low to reach saturation within a reasonable timeframe. Maximum change in mass is around 0.42 g/g-activated carbon, independent of the temperature used. However, the dependency of growth rate upon temperature is not unusual for such an infiltration process and can be explained by the Arrhenius model (Eq. (1)) which predicts that growth rates becomes larger with increasing temperature, resulting in steeper slopes.

For the deposition on a flat substrate $A$ is usually constant. In that case a linear increase of mass with time would be expected. The situation is different for infiltration into porous solids where the surface area is decreasing due to the gradual filling of pores. Therefore, the growth rate is decreasing with time and the infiltrated mass shows saturation behavior as the remaining surface area becomes negligibly small compared to its initial value. It is worth to mention that the maximum loading of 0.42 g/g-ac is independent of infiltration temperature as being analyzed experientially up to 869 K.

At 1096 K (Fig. 1b), the growth mechanism is completely different; strong particle formation is observed, resulting in

Download English Version:

https://daneshyari.com/en/article/7852443

Download Persian Version:

https://daneshyari.com/article/7852443

Daneshyari.com