

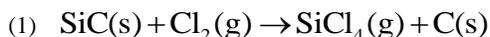
CARBON FOAMS WITH TUNABLE MICROSCOPIC AND MACROSCOPIC PROPERTIES

Tilman Knorr and Bastian Etzold

Chair of Chemical Reaction Engineering
Friedrich-Alexander-Universität
Egerlandstraße 3, D-91058 Erlangen, Germany

Introduction

Porous carbon materials are applied widely in industry. Activated carbon for example is used as an active or inert support for catalysts since decades. A relatively new class of carbon materials are the so called carbide-derived Carbons (CDC) [1, 2]. Carbide-derived carbons are obtained by the selective extraction of the metal from a carbide in a chlorine containing gas. Due to the thermodynamic stability of the metal chlorides the carbon remains as a solid [2]. Depending on the carbide the etching is carried out at temperatures in the range of 400 °C to 1200 °C. Among the large number of carbides used to process CDCs a widely used precursor is SiC. The general reaction equation of SiC with chlorine is:



The CDC-materials offer large specific surface areas up to 2000 m² g⁻¹ which can be increased by additional activation [3]. The pores of the CDC materials are mainly in the region of micropores according to IUPAC nomenclature and can be adjusted by the conditions of the CDC process [1, 4]. Thereby the temperature of chlorination and the choice of precursor carbide offer the possibility to tune the resulting pore size.

Several applications for these new CDC-materials are studied at present such as catalysis, gas storage or membranes. Using CDC-materials as catalyst support, it can be assumed that the narrow pore size distribution can induce shape selectivity [5].

Intention of the work

Ceramic foams consisting of SiC where chlorinated to achieve a carbon foam with a hierarchically structure. The carbon foam combines the advantages of the CDC-materials such as high specific surface areas and tunable pore sizes with the high thermal conductivity and low pressure drop of monolithic catalysts if compared to a fixed bed.

These aspects should make them to an interesting support for catalysts. By variation of the chlorination time, different layer thicknesses of CDC on top of the remaining carbide result. The schematic process route from the SiC precursor to a carbon foam with nonporosity is shown in Fig. 1.

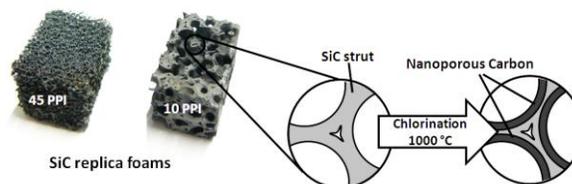


Fig. 1: Process route from carbide foam to hierarchically structured carbon foam.

Experimental

SiC ceramic foams (Fraunhofer IKTS, Germany) with two different porosities (10 pores per Inch, $\varepsilon = 0.62$ and 45 pores per Inch, $\varepsilon = 0.92$) where chlorinated at a temperature of 1000 °C in a horizontal tubular furnace.

The conversion of the carbide was determined gravimetric by balancing the sample before and after chlorination. The chlorination was carried out under constant gas velocity ($u = 1.5 \text{ cm s}^{-1}$) and chlorine concentration ($c_{\text{Cl}_2} = 1.0 \text{ mol}_{\text{Cl}_2} \text{ m}^{-3}$, diluted in He). The chlorination time varied from 30 min to 435 min for the 10 PPI foam and from 15 min to 60 min for the 45 PPI foam respectively.

The specific surface areas as well as the pore size distributions of the CDC-materials where determined by N₂- and CO₂-sorption measurement (Quantachrome QuadrasorbSi-MP and Nova 4200e). The evaluation of the sorption measurements was carried out using the NL-DFT model for carbons (software QuadraWin 4.01 and NovaWin 10.0) for pore size distribution as well as multipoint-BET (Brunauer, Emmett, Teller) for the specific surface area.

The mechanical stability of the samples was determined by compression tests on an Instron 5565 universal testing machine. Therefore the SiC foams were cut into equal block-shaped samples before chlorination. For the characterization of the samples the braking stress was taken from the measurements as a number for the mechanical stability.

Results and Discussion

Fig. 2 shows the development of the conversion at different chlorination times for both foams. Assuming the same mass depended rate approach, the reaction progress of both foams can be calculated using a first order power law (a semi batch-wise operated cascade model was used). The constant of the first order reaction rate was determined for both foams together using the least squares method.

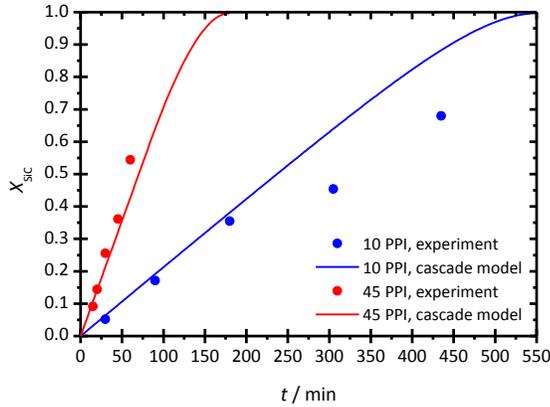


Fig. 2: Conversion vs. time for the two different SiC foams.

Small amounts of the 45 PPI foam material have been chlorinated to different conversions. Afterwards N_2 -sorption measurements were performed to determine the specific surface area as a function of the conversion. The development of the surface area is shown in Fig. 3 and matches the theoretic one [6].

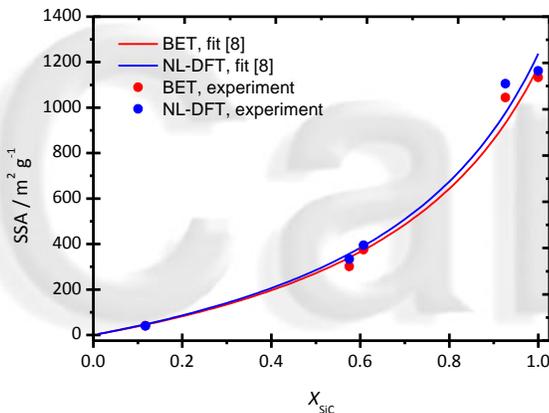


Fig. 3: Specific surface area from BET and NL-DFT evaluation of N_2 -sorption measurements for the 45 PPI foam. The fit was done according to Becker et al. [8].

The poresize distribution of the CDC-material obtained from the SiC foams was evaluated from N_2 and CO_2 -sorption. No mesopores and a typical trimodal micropore distribution for SiC derived carbon is seen.

As a quantity for the mechanical stability the breaking stress was measured for samples with different degree of conversion. In Fig. 4 one can see that a coherent decrease in the breaking stress is obtained which indicates that an optimization depending on the application is possible and required.

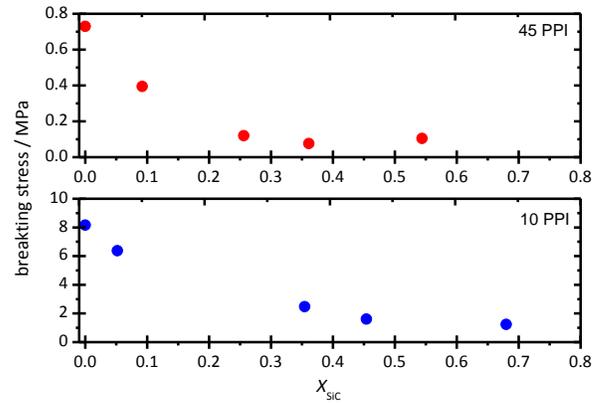


Fig. 4: Breaking stress from compression tests for different degrees of conversion.

Conclusion

We could show that the synthesis of porous carbon foams via the CDC-method is possible. The specific surface areas as well as the pore size distribution are in the expected range. Compression tests show a clear connection between mechanical stability and conversion as well as specific surface area respectively.

Acknowledgements

This report is based on a project which was funded by E.ON AG as part of the E.ON International Research Initiative. Responsibility for the content of this publication lies with the author. The authors gratefully acknowledge the funding of the German Research Council (DFG), which, within the framework of its 'Excellence Initiative', supports the Cluster of Excellence 'Engineering of Advanced Materials' (www.eam.uni-erlangen.de) at the University of Erlangen-Nuremberg.

References

- [1] Gogotsi Y, Nikitin A, Ye H, Zhou W, Fischer JE, Yi B, et al. Nanoporous carbide-derived carbon with tunable pore size. *Nat Mater.* 2003;2(9):591-4.
- [2] Zinovev AV, Elam JW, Moore JF, Hryn JN, Auciello O, Carlisle JA, et al. Coating of SiC surface by thin carbon films using the carbide-derived carbon process. *Thin Solid Films.* 2004;469-470:135-41.
- [3] Osswald S, Portet C, Gogotsi Y, Laudisio G, Singer JP, Fischer JE, et al. Porosity control in nanoporous carbide-derived carbon by oxidation in air and carbon dioxide. *Journal of Solid State Chemistry.* 2009;182(7):1733-41.
- [4] Jänes A, Thomberg T, Kurig H, Lust E. Nanoscale fine-tuning of porosity of carbide-derived carbon prepared from molybdenum carbide. *Carbon.* 2009;47(1):23-9.
- [5] Glenk F, Knorr T, Schirmer M, Gütlein S, Etzold BJM. Synthesis of Microporous Carbon Foams as Catalyst Supports. *Chemical Engineering & Technology.* 2010;33(4):698-703.
- [6] Becker P, Glenk F, Kormann M, Popovska N, Etzold BJM. Chlorination of titanium carbide for the processing of nanoporous carbon: A kinetic study. *Chemical Engineering Journal.* 2010;159(1-3):236-41.