Microreactors for Gas Liquid Solid reactions – Novel Catalyst Support Based on Carbon Nanofibers

Digvijay B. Thakur[1], Roald M. Tiggelaar[2], Han Gardeniers[2], Leon Lefferts[1] and K. Seshan*[1]
[1]*Catalytic Processes and Materials,* [2]*Mesoscale Chemical Systems*
University of Twente, P.O.Box 217, 7500 AE Enschede, The Netherlands
*K.Seshan@utwente.nl

Introduction

Currently, there is tremendous interest in the field of micro-structured gas-liquid contactors containing modified catalytic coatings on its micro-structured internals (Fig. 1) [1]. The most recent trend in the design of three-phase catalytic microreactors focuses on the use of structured catalyst supports, *i.e.* that the catalyst has to be deposited on a rigid, orderly arranged support body.

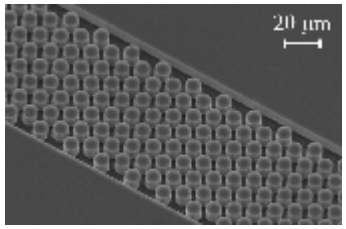

Figure 1. SEM image of flow channel in silicon with arrays of micropillars.

Catalytic support layers based on carbon nanofibers (CNFs) offer a novel option to facilitate this task [2-4]. With their inherent high surface-to-volume ratio carbon nanofibers provide tremendously high surface area [2], thereby offering the possibility to anchor high concentration of catalytic sites per unit volume. The diameter and length of the fibers can be manipulated to increase void volume and enhance the hydrodynamic accessibility of the catalytic sites. This minimises internal diffusion limitations and prevent concentration gradients inside the CNF layer In this work, synthesis of well-attached CNF layers on flat substrates, microchannel wall surfaces, is attempted in order to prepare smart microreactors for efficient gas liquid solid reactions.

Materials and Methods

Fused silica and silicon substrates were used. Nickel metal thin-films were deposited on these substrates to synthesize CNF. Ti, W and Ta were used as adhesion underlayers. Metal layers were deposited using evaporation or sputtering methods. A Thermal Catalytic Chemical Vapor Deposition (TCCVD) process using hydrocarbon gas (*i.e.* ethylene) allowed synthesys of CNF from nickel. CNF layers synthesized were characterized by HR-SEM, TEM and Raman spectroscopy to analyze their morphology, nanostructure and crystallinity, respectively. The CNF layers were also subjected to air and water flows to evaluate their stability under reaction conditions.

Results and Discussion

Samples without adhesion under layers exhibited instability of the Ni layer during pre-conditioning (dicing, reduction, and fiber growth). Presence of, e.g. a Ti adhesion layer, improved the stability of Ni film. Subjecting this stable sample to TCCVD of ethylene at 635 to 700 °C resulted in extensive growth of entangled CNFs. The CNF layer was intact but peeled off from the substrate resulting in a carpet. Detailed investigation of this carpet revealed that the thermal instability of the Ti film at elevated temperatures led to its diffusion into the Ni film, reducing adhesion and CNF carpet formed, though intact was detached from the substrate.

This problem was successfully resolved by using Ti-W and Ta as adhesion materials. In both cases well-attached layers of CNFs, about 3.5 µm thickness, were obtained with entangled morphology. The fibers showed tip- type growth with Ni particles at the tip of the fibers (HR-SEM). HR-TEM analysis showed stacked grapheme platelets containing numerous interstitial defects in the nanostructure of fiber. Raman spectrum indicated presence of disordered graphite within the CNF material (Fig. 2).

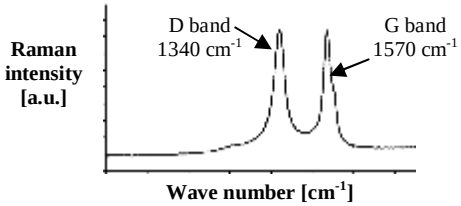

Figure 2. Raman spectrum of a CNF- layer synthesized on 25 nm Ni/10 nm Ta

Fluid flow tests showed strong attachment of synthesized CNF layer to the substrates (with a one time loss of 6 wt% mostly due to loose fibers). Surface area measurements denoted sufficiently high value of around 87 m^2/g, illustrating possible application of CNF layers as structured catalyst support.

Significance

It is expected that synthesis of stable layers of entangled carbon nanofibers on flat substrates will allow us to (i) integrate a structured support layer inside microchannels for carrying out appropriate catalytic multi-phase reactions in microreactors. (ii) incorporate catalytic centres on these supports (Fig. 3) [5] and help in the design of a smart microreactor for efficient catalytic conversions during gas liquid solid reactions.

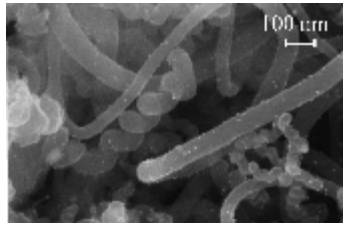

Figure 3. HR-SEM image of catalytic Pd-particles anchored on CNFs [5]

References

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