

Development and application of carbon nanofibers based nanostructured catalyst support layer for microreaction systems

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Introduction

Carbon materials have been attracting attention as potential catalysts support materials in heterogeneous catalysis due to their unparalleled flexibility in tailoring catalyst properties to specific needs [1]. Preparation of carbon nanostructured materials such as carbon nanofibers (CNFs) and/or tubes (CNTs) and exploration of their prospect toward novel catalytic applications has been of great importance to the scientific community [2]. One such field of application has seen recently a surge in research on investigating the use of nanostructure carbon materials as structured catalyst support for microreaction systems. Currently, there is tremendous interest in the use of microreactors especially for multiphase (fluid-solid) chemical reactions [3], because they feature significant enhancement in interfacial area in multiphase flows, enhanced heat (safety) and mass transfer (kinetic control) properties; all achieved due to very small dimensions of the internal structures (such as microchannels) of microreactors. However, integration of a solid catalytic phase in such reactors is a formidable task. Commonly used options [4] are, (i) using a micro packed-bed of powdered catalyst particles or (ii) thin layer catalyst coatings on reactor walls. These options limit efficiency of catalyst use, in the former case microporosity limited mass transfer and pressure drop are issues, while thin catalyst coating offer limited catalytic sites and hence low catalytic activity.

Incorporation of solid nanostructural elements in the microreactors, that can support catalytic phase, offer a way to overcome these problems because (i) microporosity and related diffusion limitations are minimized [5], (ii) the resulting high surface-to-volume ratios [6], provide enhanced interface crucial for accelerating multiphase reactions. In this work we show development and suitability CNFs, to overcome the problems stated above. The prepared materials (*i.e.* Ru/CNF in microreactor) were tested for catalytic reduction of bromate, which is one of the ozonation by-products in a drinking water treatment and a possible carcinogen [7].

Experimental

Silicon substrates, (<100>-oriented, p-type), *e.g.*, 1×1cm² flat substrates, 3×0.1 cm² microchannels, were used. Nickel/Tantalum (Ni/Ta; 25nm/10nm) layers were deposited using electron-beam evaporation. The samples were reduced in 20% H₂/N₂ at 650 °C for 1 h and then exposed to 25% C₂H₄/N₂ (or C₂H₄/H₂/N₂) for 1 h to form CNF layers. Samples

with CNF layers were refluxed in nitric acid (65 wt%) at 90 °C for 30-120 minutes. Homogeneous deposition precipitation (HDP) and pulsed laser deposition (PLD) were used to deposit ruthenium. In case of HDP, RuNO(NO₃)₃.nH₂O was used. For PLD, the details of Ru target used are: size 0.25 cm², target-substrate distance 45 mm, spot size 1 mm², Fluency 5 J/cm², at room temperature. Samples after deposition were heated at 500 °C for 90 minutes under 20% H₂/N₂ stream. The bromate reduction reaction was carried out using a polymer holder in which the microreactor chip was enclosed and provided with fluid flow connections. The bromate concentration in aqueous solution was varied between 384 mg/L (3 mmol/L) and 1280 mg/L (10 mmol/L). Syringe pump was used to flow liquid through the microreactor module using flexible fused silica capillary tubing. Bromate concentrations, initial and post reaction, were measured using flow cell (optical path = 5 mm) by UV-Vis-NIR spectrometer (Ocean Optics HR4000 High-Resolution Fiber Optic Spectrometer) equipped with deuterium and tungsten-halogen light sources. The conversion levels of bromate ions were determined by recording the subsequent decrease in absorbance at $\lambda = 230$ nm, due to the reduction of bromate ions. The catalytic experiments were also performed for Ru supported on microporous activated carbon support material to illustrate the better catalytic performance of CNF supported catalyst material for the same reaction.

Results and Discussion

A well-attached CNF layer with entangle morphology was synthesized on flat silicon based substrates (model systems representing microchannel wall surface). The reduction pretreatment resulted in a dewetting of as-deposited Ni thin film (Fig. 1a) forming Ni nanoparticles (Fig. 1b) which further act as nucleation sites for CNF growth during thermal-

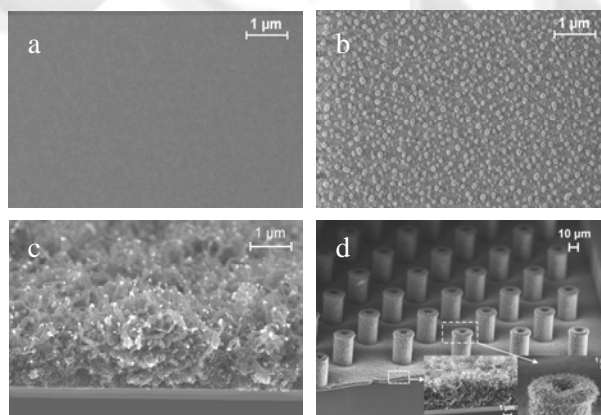


Fig. 1 SEM images showing (a) as-deposited Si-based flat substrate with Ni thin film, (b) formation of Ni nanoparticles after annealing in reducing atmosphere at 650°C, (c) CNF layer synthesized on Si-based flat substrates, (d) CNF layers synthesized in structured microchannels.

chemical vapor deposition of ethylene gas at elevated temperatures. The produced CNFs exhibited entangled morphology with tip-type growth mode (Fig. 1c). Using the same

growth condition, we were able to synthesize CNF layers covering the surface of microchannel walls as well as that of an array of pillars as shown in Fig. 1d.

CNF essentially consists of SP^2 hybridized carbon present in graphene planes connected in a hexagonal network. They are hydrophobic. In order to deposit active phase (such as ruthenium) *via* HDP from aqueous phase it is essential to modify fiber surface to be more hydrophilic. This can be achieved by oxidation to create surface oxygenate functional groups prior to deposition of Ru on them. Oxidation of CNF with nitric acid results in variety of functional groups. This is confirmed by the XPS spectra (Fig. 2), showing oxygen containing groups (dominantly carboxylic and hydroxyl).

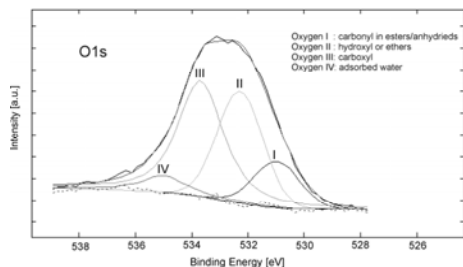


Fig. 2 XPS spectra of O_{1s} peak of the oxidized CNFs

Additionally, contact with nitric acid also allows removal of Ni used for CNF growth.

Ruthenium deposition *via* HDP and PLD techniques, on the oxidized CNF resulted in well dispersed metal particles. Ru nanoclusters in the range 1-2 nm on the CNF in the microreactors can be seen in Fig. 3. In comparison to HDP, PLD method allows precise control of the amount of metal loaded. Higher loadings are also easier to achieve.

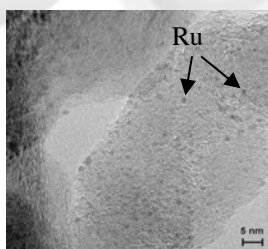


Fig. 3 TEM image showing well-dispersed Ru catalyst on CNF support prepared by homogeneous deposition precipitation.

Reduction of bromate, a contaminant in drinking water, can be achieved catalytically using Ru based catalyst materials. When tested Ru/CNF catalyst layers integrated in microreactor module showed significant catalytic activity towards bromate reduction. In addition, considerable improvement in bromate reduction levels was achieved when compared to the microporous support materials such as activated carbon (Fig. 4). This improvement can be attributed to the better accessibility of Ru active sites for bromate ions in the case of CNF supported catalyst materials due to absence of microporosity.

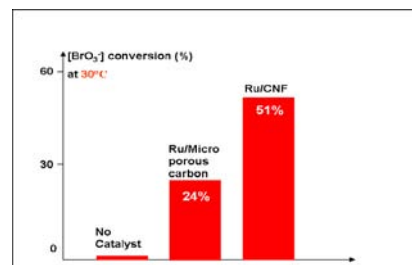


Fig. 4 Bromate conversions obtained at 30°C using Ru/Activated carbon (a microporous support), and Ru supported on CNFs.

Conclusions

Well-attached CNF layers with entangled morphology can be synthesized effectively on structured internals of microreactors using Ni thin films. These layer can be functionalized using nitric acid creating variety of oxygen-containing groups as an anchoring points for depositing active phase, particularly useful for aqueous phase preparation methods such as HDP. Both HDP and PLD are very promising techniques to deposit well dispersed metal particles catalyst metal particles on structured CNF-based support layers with narrow size distributions. Ru/CNF layers in microreactors show promise towards catalytic reduction of bromate. It is expected that this novel approach of constructing microreactors comprising stable and well-defined layers of carbon nanofibers as a structured catalyst support will allow efficient use of catalysts in fluid-solid reactions carried in microreaction systems.

Acknowledgments. Financial support from MicroNed project SMACT-2G-II&III is gratefully acknowledged.

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