Ruthenium catalyst on carbon nanofiber support layers for use in silicon-based structured microreactors, Part I: Preparation and characterization

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ABSTRACT

The preparation and characterization of ruthenium catalytic nanoparticles on carbon nanofiber (CNF) support layers *via* homogeneous deposition precipitation (HDP) and pulsed laser deposition (PLD) is presented. Prior to ruthenium deposition the CNF layers were functionalized *via* liquid phase oxidation treatment using nitric acid at 90 °C. This acid treatment not only effectively removed accessible CNF-growth catalyst, but also resulted in the formation of oxygen containing functional groups on the external surface of CNFs. A variety of characterization techniques, *viz.* TEM, XRD, XRF, XPS, and point-of-zero-charge (PZC) measurements were used to analyze the influence of the oxidation pretreatment on physico-chemical properties of CNF layers qualitatively and quantitatively. HDP yielded a very sharp size distribution (∼85% of the particles had a diameter of 1.0–1.5 nm), whereas PLD had a less narrow distribution (the diameter of ∼75% of the particles was 1–3 nm). Both methods yielded a ruthenium loading of 2.3 ± 0.1 wt.%, and in particular HDP showed uniform anchoring of particles throughout the thickness of the CNF layer. Using optimal conditions, the space in a silicon-based microreactor channel was efficiently filled with open, entangled CNF layer, which were used as anchor points for Ru using HDP and PLD.

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1. Introduction

Microreactors have received a great deal of attention in recent years [1,2]. They are miniaturized continuous flow reaction systems or reaction vessels with typical channel or chamber widths in the range of 10–500 μm [1]. Smaller diffusion distances in microreactors result in enhanced mass transfer rates and allow reactions to be carried out more efficiently. Microreactors also have high surface area-to-volume ratios ($\sim 10^4$ m^2/m^3) that lead to improved heat transfer rates, and hence safer operation conditions, *e.g.*, avoidance of thermal runaways in case of highly exothermic reactions [2,3]. These benefits are advantageous for the production of, for example, fine and/or specialty chemicals, which often involves multiphase reactions (fluid-solid) where the solid phase is mostly a catalyst. However, the integration of a solid catalytic phase (heterogeneous catalyst) in multiphase microreactors is a challenging task.

There are two ways which are explored previously for incorporating a solid phase catalyst inside the microreactor channels: (i) by using a micro-packed bed of powdered catalyst, and (ii) by using a thin layer of catalyst coated on the inner wall of a microchannel [2–8]. In the first case, high pressure drop(s) across the packed bed and diffusion limitations might arise, whereas in the latter case the thin catalyst coating usually fails to efficiently utilize the entire volume of the reactor channel. Most of these problems can be overcome by introducing nano- and/or microscale structural features in the microchannels. An attractive option is the use of carbon nanostructures onto which catalyst clusters are deposited, *e.g.* Ru, Pd or Pt metal particles.

Since the landmark paper by Iijima in 1991 [9], carbon nanostructured materials such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have generated tremendous interest due to their exceptional mechanical, electrical, physical and chemical characteristics [10–13]. One promising application is the use of carbon nanostructures as catalyst support. They offer numerous advantages over conventional supports, *viz.* (i) corrosion resistance to acid or base medium, (ii) sufficiently high surface areas and absence of micro porosity, and (iii) easy recovery of precious metal catalysts supported on them by simply burning the carbon skeleton [14–16], moreover it has also been claimed that performance of CNF supported catalyst can be influenced by adsorption of reactants on the CNF support. For example, for the liquid phase hydrogenation of cinnamaldehyde over Pt/CNF catalyst it was demonstrated that catalytic action of Pt is influenced by the amount of cinnamaldehyde adsorbed on the support in the vicinity of Pt particles [17,18].
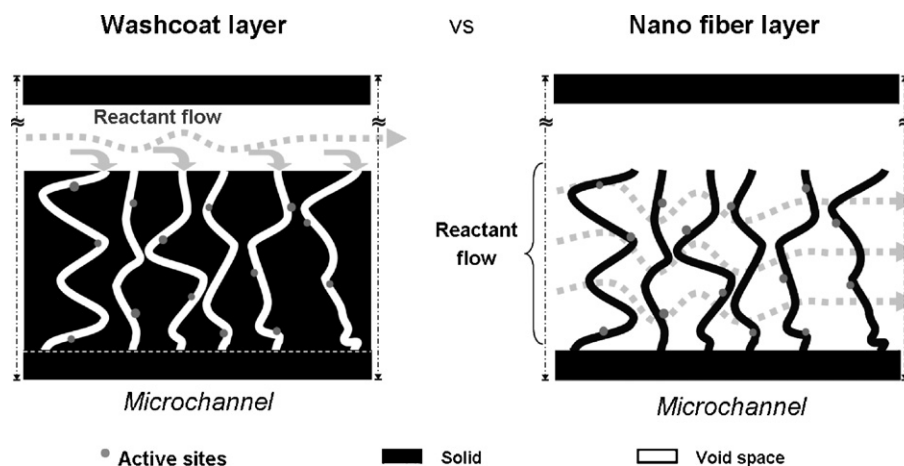
Washcoat layer vs **Nano fiber layer**

Fig. 1. A schematic representation of reactant flow inside microchannel coated with washcoat layer (left) *versus* carbon nanofiber layer (right) illustrating virtually reverse configuration in term of accessibility of the supported active sites.

The synthesis of carbon nanostructures can be achieved *via* a variety of techniques, of which details are reported elsewhere [19–26]. The catalytic thermal chemical vapor deposition (C-TCVD) method uses metals (*e.g.* Ni, Co, Fe) to catalyze CNF-growth from "C" containing gases (*e.g.* C_xH_y and CO) [19]. C-TCVD is a versatile technique and a relatively cheap method for large scale applications [19–21,27]. Fig. 1 exemplifies the advantages of integrating a layer of carbon nanostructures in a microreactor channel as an alternative to a washcoated layer. A CNF layer has easier accessibility of active sites for reactant molecules due to its open structure, as a consequence of which diffusion problems are avoided [22,23].

There are, however, critical issues in incorporating CNF layer as catalyst support in microreactors. The most important issues are the attachment of the CNF layer to the microreactor channel walls, and the deposition of stable and well dispersed active metal particles on the CNF layer. We have shown previously that a vapor deposited nickel layer can be stabilized with an adhesion layer of tantalum. In presence of C_2H_4 around 635–700 °C, well attached CNF layers can be formed on fused silica and oxidized silicon substrates [24–26]. These CNF layers, typically with thickness of 10–20 μm and fiber diameters in the range 20–70 nm, are suitable for incorporation in microchannels [26].

In this work, we address the issue of anchoring catalyst clusters, *i.e.* ruthenium nanoparticles, on CNF layer by means of homogeneous deposition precipitation (HDP) and pulsed laser deposition (PLD). Supported metal catalysts are often prepared *via* liquid phase based techniques such as impregnation. Though impregnation is the most common technique, desired active phase distribution, loading and/or dispersion cannot always be achieved with this technique. Homogeneous deposition precipitation is regarded as one of the alternative technique for impregnation. It is believed that this technique yields higher loading while maintaining good dispersion of active metal [28]. This motivated to opt for HDP as an aqueous phase deposition techniques to prepared CNF supported catalyst layers. On the other hand, CNF growth metal (Ni) thin film was deposited on silicon substrates using physical vapor deposition based technique, *i.e.* electron-beam evaporation. This inspired us to investigate suitability of similar technique (*e.g.* pulsed laser deposition) for the deposition of catalytic active phase, *i.e.* ruthenium in this case, on CNF layers. Deposition experiments and analysis are performed on oxidized silicon samples as well as with silicon-based microchannels containing ordered arrays of cylinders. The latter are to be used as microreactors for aqueous phase catalytic reduction applications.

2. Experimental

2.1. Fabrication of flat samples and microchannels with arrays of cylinders

Flat samples of 10 mm × 10 mm and microchannels were prepared from standard silicon substrates (⟨100⟩-oriented, p-type, resistivity 5–10 Ωcm, 100 mm diameter, thickness 525 μm, single side polished; Okmetic, Finland). Channels of 30 mm × 1 mm contained ordered arrays of cylinders arranged on an equilateral triangular grid. Prior to processing, the silicon substrates were cleaned by immersion in fuming 100% nitric acid (10 min) and boiling 69% nitric acid (15 min), followed by quick dump rinsing in de-mineralized water and dry spinning. In case of microchannels standard UV-lithography was used to define the pattern in 1.7 μm thick photoresist, which was postbaked for 30 min at 120 °C (in air) after development. The photoresist acted as a masklayer during deep reactive ion etching (DRIE; Adixen AMS 100SE) of silicon with a Bosch process, *i.e.* a cyclic process which uses sulfur hexafluoride for etching of silicon and octa-fluoro-cyclobutane for sidewall passivation [29]. An etchtime of *ca.* 13.5 min was required for 40–45 μm high cylinders (outer diameter 20 μm, inner diameter 10 μm; pillar spacing 20 or 50 μm). Post to etching the mask was stripped with an oxygen plasma and immersion in 100% nitric acid, followed by rinsing and drying. Fluorocarbons resulting from the DRIE process were removed by a wet oxidization step (30 min, 800 °C), followed by immersion in 1% hydrofluoric acid (1 min), rinsing in DI-water and drying. A second wet oxidation step (45 min, 1000 °C) was used to deposit a ~250 nm thick SiO_2 layer on the etched microchannel. This latter oxidation step was also used for the preparation of flat samples.

Thin films of nickel/tantalum (25 nm/10 nm) were deposited on the oxidized substrates using electron-beam evaporation (Balzers BAK600 system). In case of substrates with etched microchannels a home-built stainless-steel shadow mask was used to deposit Ni/Ta in the channels. The purity of the Ni target material was 99.99%, and >99.95% for Ta. Evaporation rates (at pressures below 10^{-7} mbar) were in the range 1–5 Å/s for Ta and 10–15 Å/s for Ni. The thicknesses of evaporated films were controlled using an in situ thickness monitor [25]. Finally, the substrates were diced into samples of 10 mm × 10 mm (flat samples) or 35 mm × 5 mm (microchannel samples) (Disco DAD-321 dicing machine).