

## Carbon nanofibers grown on metallic filters as novel catalytic materials

(Auf Metallfilter geträgerte Kohlenstoff-Nanofasern als neuartige Katalysatoren)

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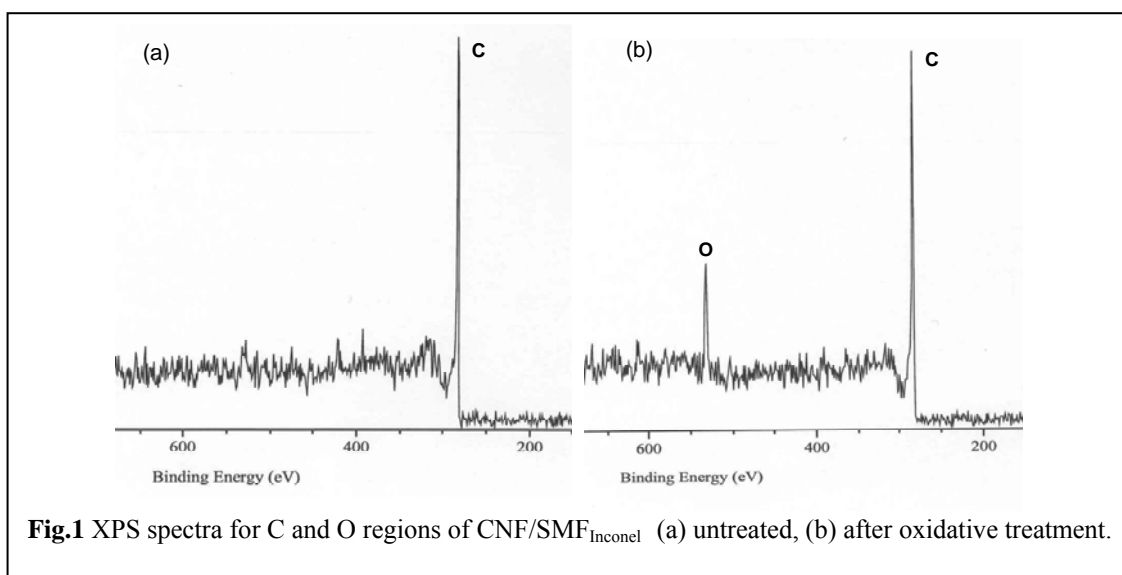
Catalytic beds with a regular arrangement are known as “structured catalysts” (monoliths, grids, woven fibers, regular porous media, etc.); they were developed to overcome problems related to the randomly packed catalyst bed, such as high pressure drops, gas channeling, agglomeration of the powder, and mechanical erosion.

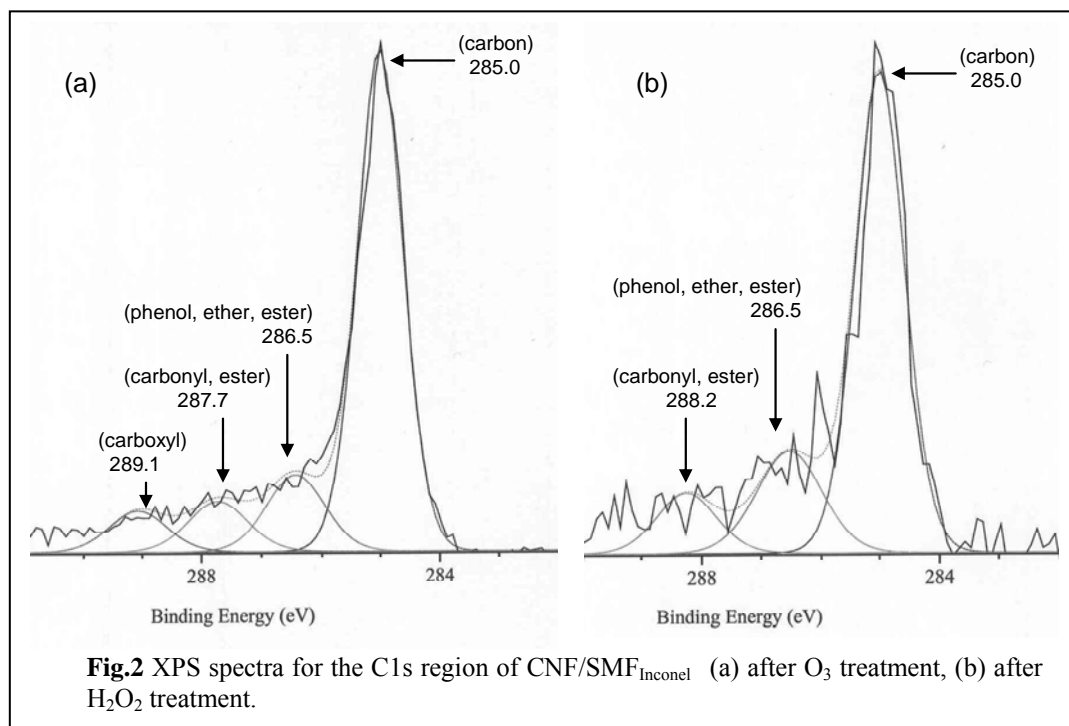
The material to study in this project consists of carbon nanofibers (CNF) grown on the surface of sintered metal fibers (SMF). The SMF act as support and as catalyst for the growth of CNFs, which remain well anchored to the filter. The macroscopic shape of the resulted composite material is suitable for the fixed bed technology and the mesoporous structure created by the network of CNFs improves the catalytic performance of the supported catalytic phase. The novel catalytic materials were tested with two different model reactions:

- the hydrogenation of acetylene over supported Pd-particles
- the use of CNF/SMF for supported ionic liquid phase catalysis

### CNFs activation and characterization

The effect of oxidation of CNF/SMF<sub>Inconel</sub> composite has been studied. Sets of experiments were performed changing the oxidizing agent: in the first case supports were activated in a 35% H<sub>2</sub>O<sub>2</sub> boiling aqueous solution for 4 hours, and then washed with water until neutral pH was attained. In the second case, the supports were treated for 30 minutes with plasma-generated O<sub>3</sub> formed in a dielectric barrier discharge plasma reactor. The





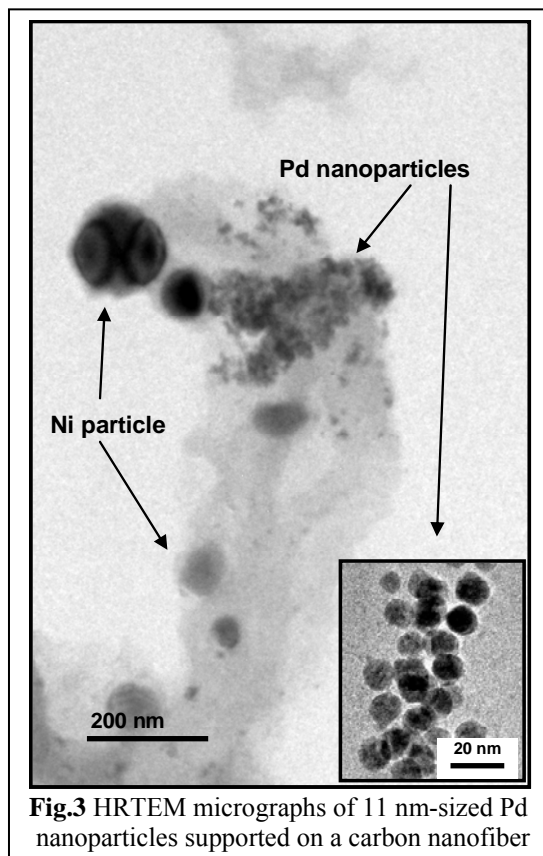
functional groups created by the oxidative treatment on CNFs/SMF<sub>Inconel</sub> composite were subsequently characterized by temperature-programmed decomposition (TPD) in He and by X-ray photo-electron spectroscopy (XPS) analysis. Both the total oxygen content as well as the number of acidic groups has been found dependent on the type of oxidative treatment as shown in Figures 1 and 2.

### **CNFs/SMF<sub>Inconel</sub> supported Pd nanoparticles for acetylene hydrogenation: particle size effect and the influence of the support functionality**

Catalytic hydrogenation of unsaturated hydrocarbons over noble metal nanoparticles is structure-sensitive. A change of selectivity and a higher turnover frequency (TOF) occurs when the size of the metal particles increases. Important advances in colloidal preparation of metal nanoparticles bring new opportunities for studies on the size-effect relations. Recently, our group showed the utilization of monodispersed Pd nanoparticles isolated from a reverse microemulsion (ME) in size-effect studies of 2-methyl-3-butyn-2-ol [and 1-hexyne liquid-phase hydrogenation. A reverse ME technique allows the control of the metal particle size by the variation of the water-to-surfactant ratio.

The research work carried out has been focused on the development of catalysts for acetylene hydrogenation based on monodispersed Pd nanoparticles isolated from a ME and supported on CNFs/SMF<sub>Inconel</sub>. The characteristic of the catalysts used during the study are resumed in Table 1

ME prepared Pd nanoparticles were deposited on CNFs/SMF<sub>Inconel</sub> supports by simple impregnation from the aqueous solution, their catalytic activity was tested in a fixed-bed tubular reactor at 150°C for 6 hours on stream. Different sets of experiments were performed for studying the size effect during acetylene hydrogenation: TOF was found to increase from 15 s<sup>-1</sup> up to 24 s<sup>-1</sup> with particle size increase in the range of 8-13 nm. The catalytic activity for Pd-nanoparticles >11 nm approaches the bulk palladium, since TOF of Pd black was found to be ~27 s<sup>-1</sup>. Selectivity to ethylene was found independent on particle size confirming the “geometric” nature of the size-effect. The influence of support on the catalytic activity was investigated by comparing



**Fig.3** HRTEM micrographs of 11 nm-sized Pd nanoparticles supported on a carbon nanofiber

the initial TOF of 11 nm Pd particles supported on differently modified CNF/SMF<sub>Inconel</sub>. The initial TOF was found to decrease with the acidity increase of the CNF surface. This effect was assigned to the higher amount of O-containing functional groups which diminished the emergence of active hydrogen to the surface decreasing the catalytic activity. The by-products (ethane and oligomers) distribution was found shifted toward the ethane formation on “acidic” supports and assigned to the electronic effect induced by the O-groups on Pd nanoparticles. The deactivation of Pd due to the green oil formation was found to vary with the particle size and the presence of sulfur traces coming from AOT-surfactant used during the ME-preparation of the Pd-nanoparticles. Smaller particles (8 nm) deactivated faster than the bigger ones (11-13 nm). The catalysts containing ME-derived Pd-nanoparticles deactivated faster than the catalyst with Pd deposited by ion-exchange. Sulfur from AOT, acting as an electron acceptor, decreases the electronic density on the Pd metallic surface and increases the adsorption strength of acetylene leading to its oligomerization

**Table 1.** Characteristics of the catalysts used during the study. Dispersion was <sup>(a)</sup> calculated by statistic method, <sup>(b)</sup> measured by CO chemisorption.

Catalyst	Support	Support pretreatment	Method of preparation	Pd loading (wt%)	Pd particle size (nm)	Pd dispersion (%)	Initial TOF (1/s)
A	CNF/SMF <sub>Inconel</sub>	-	ME	0.18	8	16.9 <sup>a</sup>	15
B	CNF/SMF <sub>Inconel</sub>	-	ME	0.18	11	13.7 <sup>a</sup>	23
C	CNF/SMF <sub>Inconel</sub>	-	ME	0.18	13	11.9 <sup>a</sup>	24
D	CNF/SMF <sub>Inconel</sub>	H <sub>2</sub> O <sub>2</sub>	ME	0.18	11	13.7 <sup>a</sup>	14
E	CNF/SMF <sub>Inconel</sub>	O <sub>3</sub>	ME	0.18	11	13.7 <sup>a</sup>	18
F	CNF/SMF <sub>Inconel</sub>	H <sub>2</sub> O <sub>2</sub>	ion exchange	0.15	5.5	19.8 <sup>b</sup>	7
G	AC	-	-	10	3.2	35.0 <sup>b</sup>	6

### CNF grown on sintered metal fiber as support for ionic liquid phase catalysis

Supported ionic liquid-phase (SILP) catalysis has attracted increasing attention in chemical reaction engineering for applications in continuous-flow reactors. The SILP applies a homogeneous catalyst in a layer of ionic liquid (IL) that is confined on the surface of a solid support with high specific surface area. Although the resulting material is a solid, the active species in the IL phase acting as a homogeneous catalyst preserves its high selectivity. The advantage of SILP catalysis is the reduced amount of IL needed and its multiple reuses, being economically and environmentally beneficial. The feasibility of the SILP catalysis has been demonstrated by several authors on granulated silica randomly packed in fixed-bed reactors. Moreover, most of the reactions were liquid/solid, with only few reported on the SILP catalyst applied to gas-phase reactions.

Catalytic beds with a regular catalyst arrangement (structured catalytic beds) present multiple advantages, including a low pressure drop during the fluid passage through the reactor and an even flow distribution, allowing a narrow residence time distribution (RTD). This property is very important for complex reactions with an intermediate as a target product. It allows for high selectivity, leading to process intensification and favorable environmental impact. The sintered metal fibers (SMFs) in the form of thin plates are used in this study as structured supports for the IL phase containing a homogeneous catalyst. The SMF plates consist of micrometer-size filaments sintered into a homogeneous 3-dimensional structure. They have a high porosity (up to 80–90%) and high permeability, leading to a low pressure drop through the reactor bed. To increase the specific surface area (SSA) of the SMFs and to attain a homogeneous coverage by IL, the SMFs were coated by a layer of carbon nanofibers (CNFs). The CNF/SMF support has high thermoconductivity, suppressing hot spot formation during exothermic hydrogenation reactions.

The feasibility of the SSILP catalysis for gas-phase reactions is tested in the selective hydrogenation of 1,3-cyclohexadiene to cyclohexene as a model reaction. The reaction was

carried out in a continuous fixed-bed tubular reactor with structured catalytic bed containing a homogeneous Rh-based catalyst immobilized in IL confined on CNF/SMF. To elucidate the influence of the support on catalyst activity/selectivity, the SMFs were also coated by a thin zeolite (ZSM-5) film on which the IL phase containing Rh catalyst was deposited. Catalysts were characterized by SEM and XRD, and high-pressure  $^1\text{H}$  NMR and  $^1\text{H}\{^{31}\text{P}\}$  NMR spectroscopy was used to provide insight into the nature of the active catalytic species.

Different modified SMFs were used for IL-phase deposition, and their surface morphologies were characterized by SEM. The SEM images with different magnifications are shown in Fig. 4 and Fig. 5. As can be seen, the  $\text{SMF}_{\text{Inconel}}$  panels consist of uniform metal fibers 8  $\mu\text{m}$  in diameter, whereas the  $\text{SMF}_{\text{Fecralloy}}$  has fibers  $\sim 20 \mu\text{m}$  in diameter. Some grain boundaries can be seen on the metal surface, indicating the formation of metal oxides after SMF oxidation (Fig. 4 and Fig. 5). The surface roughness is much greater for  $\text{SMF}_{\text{Fecralloy}}$  (Fig. 5A), due to an  $\alpha\text{-Al}_2\text{O}_3$  layer of Fecralloy fibers formed during the high-temperature treatment; aluminum diffuses from the bulk toward the surface, where it is oxidized, generating oxide film. The filters present an open macrostructure with high porosity even after the coating of their surface by CNFs (Fig. 4C) or zeolites (Fig. 5C). As seen on the images of the supports and related SSILP catalysts (Fig. 4 and Fig. 5), the liquid phase completely covers the metal fibers. However, the homogeneity of the coverage depends strongly on the fiber surface morphology. On relatively smooth Inconel fibers (Fig. 4A), an excess of IL tends to form meniscuses at fiber crossing points (Fig. 4B), whereas the mesoporous layer of CNF on the metal surface (Fig. 4C) allows easy spreading, leading to uniform IL films (Fig. 4D). The same phenomenon is observed when analyzing  $\text{SMF}_{\text{Fecralloy}}$  and ZSM-5/ $\text{SMF}_{\text{Fecralloy}}$  (Fig. 5). Zeolites on Fecralloy fibers form a network in which ionic liquid can be easily deposited, resulting in a uniform film (Fig. 3D).

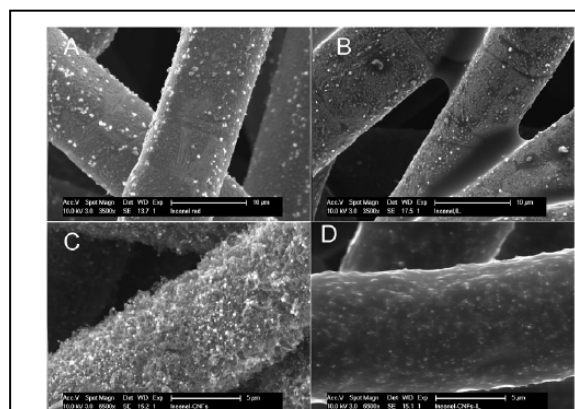


Fig. 4: SEM images of  $\text{SMF}_{\text{Inconel}}$ : A) SMF oxidized; B) IL/SMF; C) CNF/SMF; D) IL/CNF/SMF

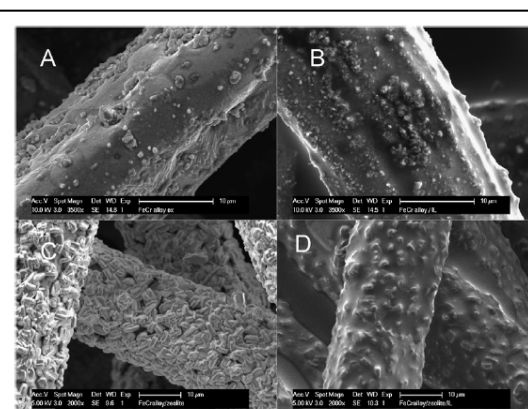


Fig. 5: SEM images of  $\text{SMF}_{\text{Fecralloy}}$ : A) SMF oxidized; B) IL/SMF; C) CNF/SMF; D) IL/CNF/SMF

The experimental results demonstrated that the IL thin film immobilized on CNF/SMF<sub>Inconel</sub> support with high thermal conductivity and large surface area ensures efficient use of the transition metal catalyst without mass-transfer limitations and under isothermal conditions during the exothermic reaction. The SSILP catalyst, [Rh(H)<sub>2</sub>Cl(PPh<sub>3</sub>)<sub>3</sub>/IL/CNF/SMF], showed high selectivity (>96%) and turnover frequency up to 250 h<sup>-1</sup> with acceptable stability during 6 h on stream.

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