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Palladium on carbon nanofibers grown on metallic filters as novel structured catalyst

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Abstract

A novel composite material based on carbon nanofibers (CNF) grown on sintered metal fibers ($SMF_{Inconel}$) filter was investigated for its favorable properties as catalytic support. The CNF were formed directly over the $SMF_{Inconel}$ by thermal (650 °C) chemical vapor deposition of ethane–hydrogen mixture. The CNF/$SMF_{Inconel}$ composite consists of metal fibers entangled by CNF network of microns thickness and strongly anchored to the metal surface. The properties of the CNF/$SMF_{Inconel}$ were controlled by the synthesis conditions. The CNF coating reduced the filter porosity and decreased the material permeability, but the pressure drop during the gas passage through the reactor remained low for CNF fraction <10%. Palladium was deposited on CNF previously activated by boiling in hydrogen peroxide. The activity and selectivity of Pd°/CNF/$SMF_{Inconel}$ catalysts were tested in the selective hydrogenation of acetylene and compared with Pd supported on activated carbon fibers (Pd°/ACF). The TOF was one order of magnitude higher for Pd°/CNF/$SMF_{Inconel}$ as compared to Pd°/ACF. This effect was attributed to a strong metal-support interaction of Pd°-nanoparticles with the graphitized CNF. The reaction was found to be structure sensitive leading to a decrease of TOF for the Pd°-particles <3 nm.

Keywords: Carbon nanofibers; Sintered metal fiber filters; Carbon/metal composites; Pressure drop; Structured catalyst; Acetylene hydrogenation

1. Introduction

The reactors with structure catalytic beds (RSCB) are considered as a valuable alternative to more traditional reactors randomly filled with catalyst particles [1,2]. The RSCB avoid flow maldistribution, hot-spots formation and high dispersion in the residence time distribution. This leads to a higher selectivity and efficiency of the process beneficial for the environment and from the economic point of view. Therefore, new materials for the RSCB are needed, able to carry out together with the chemical reaction improved mixing, heat exchange, and separation [3]. An important requirement for these materials is a low pressure drop during the gas passage through the RSCB.

Carbon nanofibers are the innovative materials that show potential as catalyst support [4]. Compared to activated carbon, CNF present a high specific surface area without microporosity, preventing mass transfer limitations. In addition, their graphitic structure leads to metal-support interaction, which can improve catalytic activity/selectivity. Up to now, the majority of catalysts based on CNF are used in the form of fine powders. It makes them difficult to handle and provokes high pressure drop through the catalytic bed. To solve this problem, CNF were grown on a suitable structured support. Vieira et al. proposed to grow CNF on graphite felt [5]. Other groups have synthesized nanocarbons directly on monoliths [6,7], carbon blacks [8,9] and on a large area of sodalime glass by CVD of acetylene [10]. But achieving strong anchoring and uniformity of CNF coating still remains a challenge, especially on metallic surfaces.

Metal supports like sintered metal fibers (SMF) present advantages due to high electro- and thermo-conductivity, regular open structure and their filtration properties. These filters consist of a homogenous 3D structure of metallic micro-filaments. They are characterized by porosity up to 80–90%, high permeability and excellent filtrating proper-

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ties with a low pressure drop through the catalytic bed during reactor operation. Fibers made of special alloys (stainless steel, Inconel, Fecralloy) exhibit high mechanical strength, chemical and thermal stability. The high thermal conductivity of the metal fibers matrix provides a radial heat transfer coefficient two-fold higher compared to randomly packed catalytic beds [11]. This results in nearly isothermal conditions when used as catalytic materials for highly exo/endothermic reactions. This fibrous matrix also acts as a static micromixer avoiding channeling.

The use of a CNF/SMF filter as a catalyst support allows to vary different parameters in order to fit the final material requirement. First of all, its macrostructure can be regulated by the choice of the starting SMF filter. The size of the metallic fibers, the porosity and the thickness of the filter are available in a broad range. Secondly, the growth of a CNF layer on the metallic fibers can be regulated to obtain the desired carbon layer thickness or the adequate specific surface area. Finally the deposition of an active component on the CNF provides the catalytic sites to the composite. This material is designed to control the structural, chemical and physical properties over multiple levels.

In our previous publication [12] the first evidence was presented for the use of SMF filters as supports for the growth of CNF. The $SMF_{Inconel}$ support containing nickel was shown to be a catalyst for the CNF growth.

This work is aimed on the study of the CNF/$SMF_{Inconel}$ composite support for Pd°-nanoparticles and the characterization of this structured catalyst. The activity of the Pd°/CNF/$SMF_{Inconel}$ was tested in the selective hydrogenation of acetylene to ethylene. Hydrogenation is an exothermic process and therefore, an efficient heat evacuation due to high thermal conductivity of CNF/$SMF_{Inconel}$ support improves the reaction performance. The Pd°/CNF/$SMF_{Inconel}$ was compared with the more traditional Pd° supported on structured activated carbon fibres (Pd°/ACF).

2. Experimental

2.1. Materials

Commercially available sintered metal fiber filter (SMF) was used as CNF support during this study:

Inconel 601, Bekipor ST20AL3 (composition: Ni: 60.5%; Cr: 23%; Al: 1.25% Cu: 1%; Mn: 1%; Si: 0.5%; C: 0.1%; S: 0.015%; Fe: balance), 8 μm fiber diameter, 0.49 mm thickness, (Bekaert Fibre Technology, Belgium).

The filter was used as received. The commercial acetylene was 99.6%, others gases were >99.995% purchased from CarbaGas, Switzerland and used as received.

The method of preparation of carbon nanofibers over Inconel sintered metal fiber filters (CNF/$SMF_{Inconel}$) was described in a previous paper [12]. All CNF/$SMF_{Inconel}$ samples were treated in an ultrasonication bath (Bransonic ultrasonic cleaner, HF-output power nom. 30 W, Branson Ultrasonics Corp., USA) in order to estimate the mechanical resistance of the composite. After a 5-min treatment in a methanol solution, no carbon came out, indicating a strong mechanical stability of the CNF on the metallic filter. The composite support was used as synthesized or activated in a 35% H_2O_2 boiling aqueous solution (Fluka, Buchs, Switzerland) during 4 h.

Activated carbon fibers (ACF) woven fabrics (AE 1101, KoTHmex, Taiwan, Carbon Technology Co.) were used as catalyst supports as described in details in [13].

The tetra-amminopalladium (II) chloride monohydrate $[Pd(NH_3)_4]Cl_2{\cdot}H_2O$ "p.a." was used as received (Aldrich Chem. Co., Reactolab S.A., Switzerland). The palladium (II) chloride anhydrous ($PdCl_2$) and the sodium chloride (NaCl) were "p.a." from Fluka (Buchs, Switzerland). The Na_2PdCl_4 was prepared by mixing equivalent amounts of $PdCl_2$ and NaCl in aqueous solution. Distilled water was used throughout the study.

2.2. Composite pressure drop measurements

Measurements of the pressure drop through the CNF/$SMF_{Inconel}$ were carried out in a tubular reactor with an internal diameter of 12 mm. One to two round slices of composite (12 mm diameter, 0.49 mm thickness) were placed in the reactor. If two pieces were used, they were separated by a 5-mm ring. The composites were pressed against a stopper by a hollow piston to avoid gas escape. The pressure drops were measured using U-tube filled by water.

2.3. Characterization of surface functional groups

Characterization of the functional groups on the CNF/$SMF_{Inconel}$ surface after hydrogen peroxide pretreatment was performed by temperature-programmed decomposition (TPD) in He (20 ml/min, ramp rate 10 K/min) using a Micromeritics AutoChem 2910 analyzer. In these experiments about 80 mg of 6% CNF/$SMF_{Inconel}$ were placed in a quartz tubular reactor. The TPD products were analyzed by a ThermoStar-200 quadrupole mass spectrometer (Pfeiffer Vacuum) calibrated using gas mixtures of known compositions. The reaction temperature was controlled by a thermocouple inserted in the catalyst bed. Previous to the TPD runs, the reactor was purged by He for 30 min at room temperature.

2.4. Preparation of Pd catalysts

Pd deposition on the CNF/$SMF_{Inconel}$ composites or on ACF was performed via ion-exchange/adsorption from aqueous solutions (0.8 l, stirred for 5 h) using two different precursors: $[Pd(NH_4)_3]Cl_2$ and Na_2PdCl_4. The concentrations of Pd in the solutions were set to attain between 2 to 5 wt.% Pd° on CNF or ACF. After Pd-ions deposition, the supports were rinsed with water, air-dried for 12 h at room temperature and finally for 15 h at 393 K.

Table 1
Characteristics of the catalysts used for selective hydrogenation of acetylene

Catalyst	Support	Support pretreatment	Pd Precursor	Pd (%)	Pd dispersion (–)	Pd particle size (nm)
A	CNF/SMF$_{Inc}$	–	Na_2PdCl_4	3.2	0.17	6.4
B	CNF/SMF$_{Inc}$	H_2O_2	Na_2PdCl_4	4.8	0.31	3.6
C	CNF/SMF$_{Inc}$	H_2O_2	$Pd(NH_3)_4Cl_2$	3.7	0.53	2.1
D	ACF	–	Na_2PdCl_4	5.0	0.54	2.1
E	ACF	–	$Pd(NH_3)_4Cl_2$	4.9	0.29	3.9

The dispersion and the size of Pd°-particles were determined by pulse chemisorption of CO at 323 K via an AutoChem 2910 instrument (Micromeretics SA, Belgium) with a TCD. The samples (200 mg) were pre-treated in a flow of H_2 (20 ml/min) at 423 K during 1 h and then kept in a flow of He (20 ml/min) at the same temperature for 1 h. A Pd surface density of 12.02 g/cm^3 and a stoichiometry factor SF_{Pd} = CO/Pd of 1.667 were taken for the SSA_{Pd} calculations. Table 1 shows the properties of different catalysts used.

2.5. *Catalytic activity measurement*

The hydrogenation of acetylene was carried out in a stainless steel jacketed tubular reactor with an internal diameter of 12 mm. The temperature of the oil was regulated by a Juvo (K.K. Juchheim Laborgeräte GmbH, Germany).

The catalyst was positioned in the reactor perpendicularly to the gas flow. Two round slices (12 mm diameter) of the catalyst were separated by a ring (5 mm thickness) and in an antechamber glass beads were placed to insure pre-heating of the reacting mixture. In this way a short contact time was obtained resulting in a differential reactor.

Before the reaction, the catalyst was activated in 10% H_2 in Ar (total 150 ml (STP)/min) at 453 K overnight and the reaction temperature was set at 423 K. Acetylene, hydrogen and argon were mixed with the ratio of 1.5:3.0:95.5 and used at a total flow of 450 ml (STP)/min. The pressure was kept constant at 1.25 atm. Products were analysed by a HP 6890 gas chromatograph using He as carrier gas, and FID and TCD as detectors. Product separation was performed using a 30 m Carboxen 1010 (Supelco) 0.25 mm capillary column.

Catalytic activity and selectivity were monitored after 8 h on stream since only after this time steady-state was attained.

3. Results and discussion

3.1. *Pressure drop through the composite CNF/SMF$_{Inconel}$*

The sintered metal fibers filters exhibit low pressure drop during gas passage due to their macro-structure and high void fraction. The growth of carbon nanofibers on the filters may change the macrostructure. Fig. 1 shows CNF/SMF$_{Inconel}$ at different magnifications. This sample has a carbon fraction of 4.8 wt.% defined by the ratio between the mass of carbon and the mass of the SMF filter. At low magnification (Fig. 1A and B), the geometry of the filter is seen to be preserved. By zooming on the filter (Fig. 1C), the roughness of the surface becomes evident. The filter's fibers are no longer smooth like for pristine filters. A 1-μm thickness of the CNF layer was estimated by difference in diameter between the metallic fiber surrounded by carbon (Fig. 1C) and the initial diameter of the filter's fibers. Morphology of individual nano-fibers is visible on Fig. 1D.

The composite material may have an increased pressure drop if the CNF layers possess a non negligible volume. The friction is known to increase due to the higher fiber roughness. To evaluate this feature, different amounts of CNFs were grown on SMF$_{Inconel}$ and the pressure drop was monitored under different flow rates. The evolution of the pressure drop with the gas superficial velocity is presented on Fig. 2 for different fractions of CNF. As expected, the pressure drop increases with the CNF content. The linear relation between the pressure drop and the superficial velocity gives the permeability factor. It follows the Darcy's law, which relates the pressure drop of a fluid through a porous layer to the superficial velocity:

$$\frac{\Delta P}{L} = \frac{1}{k}\,\mu u$$

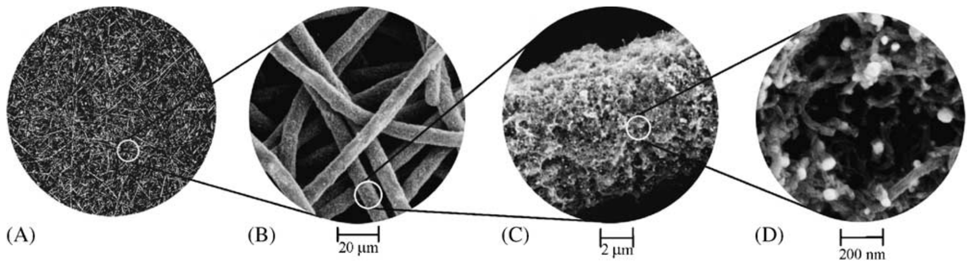

Fig. 1. Microscope images of SMF$_{Iconel}$ filters and carbon nanofibers obtained after 1 h synthesis over SMF$_{Inconel}$ at 655 °C, Ar:C_2H_6:H_2 = 85:3:17 (600 ml (STP)/min).

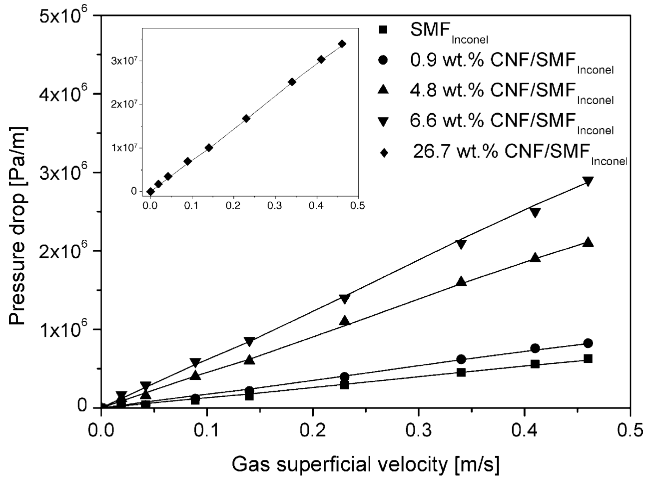

Fig. 2. Pressure drop per unit length as a function of gas superficial velocity for different CNF fractions on $SMF_{Inconel}$.

where ΔP is the pressure drop; L the thickness of the bed; μ the viscosity of the gas; u the gas superficial velocity and k the permeability factor.

On Fig. 3 the evolution of the pressure drop for a gas superficial velocity of $u = 0.4$ m/s and the permeability factor k are shown as a function of the carbon fraction (CNF in wt.%) in the composites.

The pressure drop does not increase linearly with the CNF fraction becoming more pronounced as the CNF content increases, but it remains relatively low up to 10% of CNF. The increase is due to concomitant effects of a decreasing porosity and a larger compactness of the CNF network. The permeability factor decreases drastically even for small fractions of CNF.

The specific surface area (SSA) is an important parameter for an efficient catalytic support. With the increase of the CNF amount on the filter, the SSA increases. Nevertheless, a high SSA at high CNF fraction leads to high pressure drops which is detrimental during reactor operation. Optimization of these two parameters lead to the suitable value of ~6 wt.% of CNF fraction which gave a BET specific surface area of ~29 m^2/g. This amount of CNF was sufficient to deposit Pd°-nanoparticles with high dispersion and to avoid high pressure drops. The samples with this carbon content were used throughout this study.

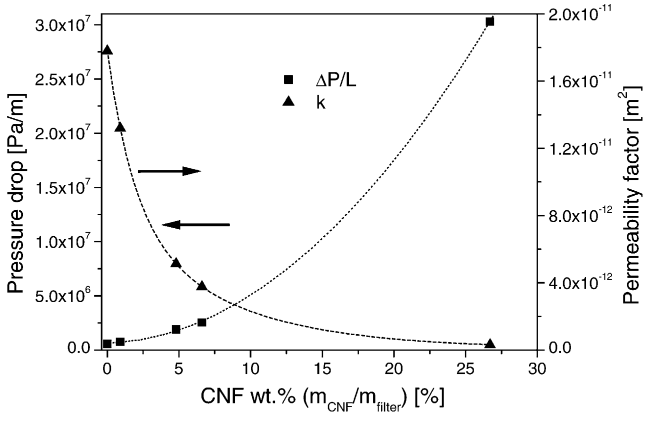

Fig. 3. Evolution of the pressure drop per unit length and the permeability factor as a function of mass fraction of CNF on $SMF_{Inconel}$ for a gas superficial velocity of 0.4 m/s.

3.2. Activation of $CNF/SMF_{Inconel}$ support

In order to achieve high palladium dispersion on $CNF/SMF_{Inconel}$, the CNF surface was activated by hydrogen peroxide to form oxygenated surface groups like phenolic, carboxylic, etc. These groups are able to anchor cationic metal precursor via ion exchange. In addition, the oxygen containing groups decrease the hydrophobicity of the carbon support and improve the metal deposition by adsorption from the aqueous solution [14]. It is well known that each surface oxygenated group decomposes to well define products, e.g., that CO_2 derives from carboxyl, lactone/lactol and carboxyl anhydride groups, and CO is formed by decomposition of carboxyl anhydride, carbonyl/quinone, phenolic and ether-type oxygen groups. Total amounts of CO and CO_2 produced during temperature-programmed decomposition (TPD) in He can be used for the quantitative and qualitative characterization of the carbon surface functional groups [15,16].

Fig. 4 shows a typical TPD profile obtained with a $CNF/SMF_{Inconel}$ support treated during 4 h in a boiling aqueous solution of H_2O_2. Evolution of CO and CO_2 indicates the formation of oxygen containing groups on CNF. The CO_2 produced at 600 K comes from carboxylic groups, and around 700 K can be assigned to the decomposition of anhydride or lactone groups [17,18]. The narrow peak of CO at ~900 K can be due to phenolic groups, and the peak at ~1050 K can be assigned to carbonyl or quinine groups [16,17,19].

Previous work of our group [20] showed that noble metal deposition on a carbon surface containing a large amount of CO_2 producing groups led to the formation of big metal particles. At the same time, the metal deposition via ion-

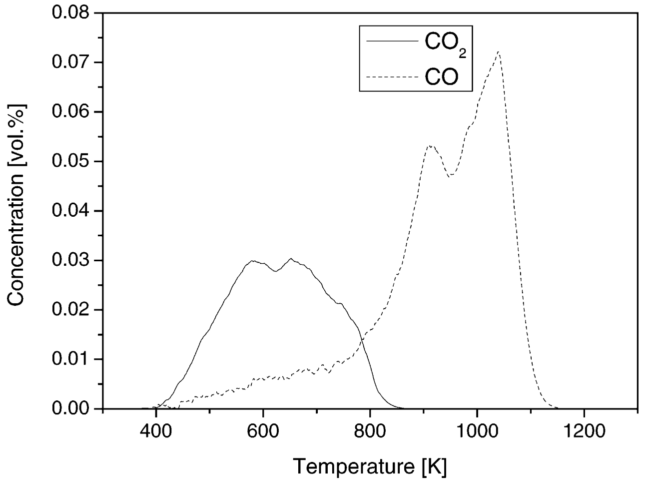

Fig. 4. Profile of temperature programmed decomposition (20 ml/min He, 10 K/min) of $CNF/SMF_{Inconel}$ activated in boiling 35% aqueous solution of H_2O_2 during 4 h.

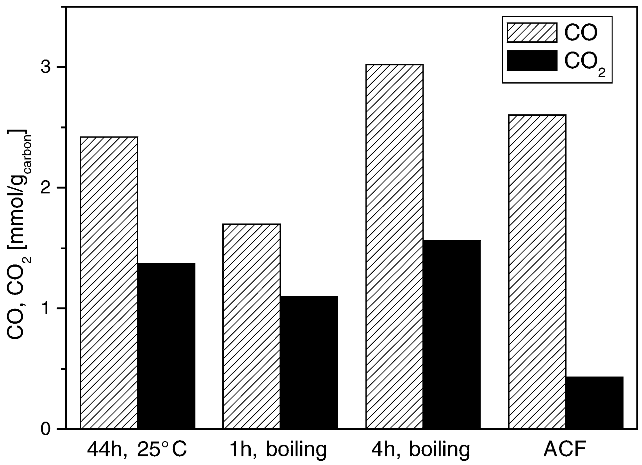

Fig. 5. Amount of CO and CO_2 obtained during TPD of non-treated ACF and CNF/SMF$_{\mathrm{Inconel}}$ treated in a 35% aqueous solution of H_2O_2 at different conditions (20 ml/min He, 10 K/min).

exchange with the more stable groups producing CO during TPD resulted in smaller metal nanoparticles.

Fig. 5 presents the amount of CO and CO_2 evolved during the TPD in He of non-treated ACF and CNF/SMF$_{\mathrm{Inconel}}$ after activation by H_2O_2. Hydrogen peroxide treatment is seen to be suitable for the activation of CNF. The H_2O_2 treatment at room temperature resulted in a formation of oxygen containing groups on the surface after 40 hours. When the CNF was conditioned with boiling hydrogen peroxide solution, one hour treatment led to the formation of about 70% of the oxygenated groups as compared to 44 h treatment at 25 °C. When the boiling treatment time was raised up to 4 h, the formation of CO producing groups almost doubled leading to a ratio CO:CO_2 of 2. Therefore, boiling in hydrogen peroxide for 4 h turned out to be a good compromise between a short time and a high concentration of surface functional groups. In comparison, the non-treated ACF was found to have less oxygen containing groups than the activated CNF. Lower amount of CO_2 producing groups on the surface of ACF (three times less than the CNF activated for 4 h) indicates a higher acidity of the CNF/SMF$_{\mathrm{Inconel}}$ support.

3.3. Palladium deposition on the structured supports

Next we focused on the effect of Pd precursor on the deposition of Pd nanoparticles. Table 1 summarizes the main characteristics of the catalysts prepared during this work. It was not possible to depose palladium using $[Pd(NH_4)_3]Cl_2$ precursor without hydrogen peroxide pretreatment indicating an ion-exchange mechanism involved in this case [21]. An interaction with the π-electron system of the CNF was not sufficient to anchor the cation. The anionic palladium precursor doesn't need surface functional groups and was deposited via adsorption on CNF/SMF$_{\mathrm{Inconel}}$. But without CNF activation in H_2O_2, the anionic precursor led to low dispersion (17%) with Pd°-particles of 6.4 nm. A highest level of 3.2% Pd was attained in this case. After treatment with H_2O_2 (see Table 1, catalyst B), it was possible to deposit 4.8% Pd with a higher dispersion (~31%) due to somehow small particles with a diameter of 3.6 nm. The ion-exchange with cationic precursor on activated CNF (Table 1, catalyst C) produced small particles of 2.1 nm. This indicates a modest palladium sintering taking place during reduction of $[Pd(NH_4)_3]^{2+}$ ion on the CNF support.

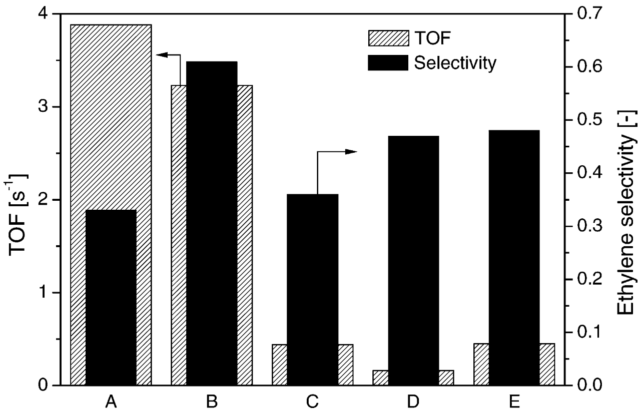

Fig. 6. Turnover frequency and selectivity towards C_2H_4 of the catalysts; 423 K, 450 ml(STP)/min (1.5%C_2H_2, 3%H_2 in Ar).

3.4. Catalytic performances of Pd/CNF/SMF$_{\mathrm{Inconel}}$

Before testing the CNF/SMF$_{\mathrm{Inconel}}$ for hydrogenation of acetylene, it was determined that the SMF$_{\mathrm{Inconel}}$ filters were not catalytically active in this reaction under the conditions used. The reaction rates for the different Pd catalysts were stated per unit of Pd mass. Values between 8×10^{-4} and 9×10^{-3} mol/g$_{\mathrm{Pd}}$ s were found, revealing differences between the catalysts activities. In order to understand these differences, reaction rate values were converted into turnover frequencies (TOF) based on the dispersion of Pd measured. Fig. 6 shows the TOFs and the ethylene selectivity for the samples presented in Table 1.

The highest TOF was observed for the CNF/SMF$_{\mathrm{Inconel}}$ support with the Pd deposited from Na_2PdCl_4 precursor. This result involves two different effects: (a) strong Pd-support interaction and (b) the reaction sensitivity to the Pd-particle size. If we compare catalysts B and E having the same particle size, the activity was more than seven-fold higher in the case of the CNF support (catalyst B). This shows the significant effect on the activity of ‘‘strong metal-support interaction’’. Graphitic nature inherent to the CNF enhances the palladium activity for hydrogenation as compared to the amorphous form of activated carbon (ACF). Electron transfer between the conductive CNF support and the palladium particles, inducing electronic perturbations of the metal could explain this activity increase [22,23].

The palladium particle size also affects the catalysts activity besides the support: there is a drop in TOF for Pd-particles <3 nm. For the same CNF support, the catalyst A compared to B, ~20% reduction was observed when the Pd particle size decreased from 6.4 to 3.6 nm. For the catalysts B compared to C, the TOF dropped on 85% when the Pd particle size changed from 3.6 to 2.1 nm. As claimed by several works in the field [24–29], the relationship between the Pd particles size and their electronic properties affects the Pd catalytic behaviour. Small particles, being electron deficient [30], adsorb more strongly electron-rich substrates, like alkynes, lowering the turnover frequency. For bigger particles, their electronic properties approach those of bulk metal, and therefore the metal–substrate interaction decreases, leading to a higher reactivity of adsorbed alkyne. Another explanation involves a change in the ratio between the different types of surface atoms [31]. As the Pd particle size decreases, the fraction of Pd surface atoms with a low coordination number (edge atoms) increases, and this modifies the catalytic properties of the metal.

Comparing the C and D catalysts, which have the same dispersion, the support nature is seen to affect the catalytic activity, enhancing the TOF of the CNF based catalyst. If the catalyst C is compared with the E sample, the influence of the support is probably compensated by the size effect, resulting in similar TOF.

The selectivity of Pd catalysts towards ethylene is known to be governed by a large difference in the adsorption strength between acetylene and ethylene [32–35]. According to Gigola et al. [25], who studied the influence of Pd particle size on the hydrogenation of C_2H_2 over Pd/Al_2O_3, a metal dispersion under 0.2 is required for a high ethylene selectivity. At contrast, Duca et al. [36] reported no influence of Pd-particle size on the selectivity to C_2H_4 for Pd/pumice catalysts. In our study, the palladium particle size can hardly be related to the ethylene selectivity, but the catalyst support seems to have an influence on the latter parameter. The catalysts based on CNF/$SMF_{Inconel}$ support presented a much higher selectivity when the CNF surface was activated by H_2O_2 (see Fig. 6, cat. B). Since this treatment modifies the acidity of the support due to the formation of O-containing surface groups, the adsorption strength of acetylene as compared to ethylene may be enhanced favoring acetylene hydrogenation. This leads to higher selectivity to ethylene. This result is in line with the results for the ACF support (see Fig. 6, catalysts D and E). The ACF was shown to possess a high amount of acid surface groups. Therefore, Pd/ACF catalysts showed a rather high selectivity. More work is needed to attain a complete understanding of this process.

4. Conclusions

- A novel composite material based on carbon nanofibers (CNF) grown on sintered metal (Inconel) fibers ($SMF_{Inconel}$) filter was shown as innovative structured catalytic support for Pd-nanoparticles.
- The pressure drop during the gas passage through the reactor filled by this catalyst was found to increase with the amount of CNF due to decrease of the filter porosity (permeability). An optimal amount of ~6 wt.% CNF gave a suitable specific surface area ~29 m^2/g of the support and a low pressure drop.
- The dispersion of palladium was controlled by pre-treatment of the CNF/$SMF_{Inconel}$ in boiling H_2O_2 and by the nature of the Pd precursor used.
- Selectivity and activity (TOF) of Pd/CNF/$SMF_{Inconel}$ catalysts were tested in selective hydrogenation of acetylene. “Strong metal-support interaction” due to the graphitic nature of CNF resulted in one order of magnitude higher TOF values when Pd was supported on CNF/$SMF_{Inconel}$ if compared to the amorphous active carbon fibres (ACF).
- The palladium particle size was observed to have a strong influence on the acetylene hydrogenation: the particles <3 nm demonstrated a low activity.
- The selectivity towards ethylene was not observed to depend on the palladium particle size but on the carbon support acidity. The selectivity increased with the amount of surface acid oxygenated groups.

Acknowledgments

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References

[1] T. Boger, A.K. Heibel, C.M. Sorensen, Ind. Eng. Chem. Res. 43 (2004) 4602.
[2] A. Cybulski, J.A. Moulijn, Catal. Rev. Sci. Eng. 36 (1994) 179.
[3] M. Grunewald, D.W. Agar, Chem. Eng. Sci. 59 (2004) 5519.
[4] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A-Gen. 253 (2003) 337.
[5] R. Vieira, C. Pham-Huu, N. Keller, M.J. Ledoux, Chem. Commun. (2002) 954.
[6] T. Vergunst, F. Kapteijn, J.A. Moulijn, Carbon 40 (2002) 1891.
[7] N. Jarrah, J.G. van Ommen, L. Lefferts, Catal. Today 79 (2003) 29.
[8] S. Lim, S.H. Yoon, Y. Shimizu, H. Jung, I. Mochida, Langmuir 20 (2004) 5559.
[9] S. Lim, S.-H. Yoon, Y. Korai, I. Mochida, Carbon 42 (2004) 1765.
[10] Y.T. Lee, N.S. Kim, J. Park, J.B. Han, Y.S. Choi, H. Ryu, H.J. Lee, Chem. Phys. Lett. 372 (2003) 853.
[11] D.R. Cahela, B.J. Tatarchuk, Catal. Today 69 (2001) 33.
[12] P. Tribolet, L. Kiwi-Minsker, Catal. Today 102–103 (2005) 15–22.
[13] D.A. Bulushev, L. Kiwi-Minsker, I. Yuranov, E.I. Suvorova, P.A. Buffat, A. Renken, J. Catal. 210 (2002) 149.
[14] F. Rodriguez-reinoso, Carbon 36 (1998) 159.
[15] M. Domingo-Garcia, F.J.L. Garzon, M.J. Perez-Mendoza, J. Colloid Interface Sci. 248 (2002) 116.
[16] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Carbon 37 (1999) 1379.
[17] B. Marchon, J. Carrazza, H. Heinemann, G.A. Somorjai, Carbon 26 (1988) 507.
[18] Q.L. Zhuang, T. Kyotani, A. Tomita, Energy Fuels 8 (1994) 714.
[19] U. Zielke, K.J. Huttinger, W.P. Hoffman, Carbon 34 (1996) 983.
[20] D.A. Bulushev, I. Yuranov, E.I. Suvorova, P.A. Buffat, L. Kiwi-Minsker, J. Catal. 224 (2004) 8.

[21] B.L. Mojet, M.S. Hoogenraad, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, J. Chem. Soc. Faraday Trans. 93 (1997) 4371.

[22] N.M. Rodriguez, M.S. Kim, R.T.K. Baker, J. Phys. Chem. 98 (1994) 13108.

[23] C. Park, M.A. Keane, J. Colloid Interface Sci. 266 (2003) 183.

[24] J.P. Boitiaux, J. Cosyns, S. Vasudevan, Appl. Catal. 6 (1983) 41.

[25] C.E. Gigola, H.R. Aduriz, P. Bodnariuk, Appl. Catal. 27 (1986) 133.

[26] Y.A. Ryndin, L.V. Nosova, A.I. Boronin, A.L. Chuvilin, Appl. Catal. 42 (1988) 131.

[27] S. Hub, L. Hilaire, R. Touroude, Appl. Catal. 36 (1988) 307.

[28] Y.A. Ryndin, M.V. Stenin, A.I. Boronin, V.I. Bukhtiyarov, V.I. Zaikovskii, Appl. Catal. 54 (1989) 277.

[29] V. Ponec, Stud. Surf. Sci. Catal. 95 (1995) 477.

[30] M.G. Mason, Phys. Rev. B 27 (1983) 748.

[31] A. Molnar, A. Sarkany, M. Varga, J. Mol. Catal. A-Chem. 173 (2001) 185.

[32] G.C. Bond, P.B. Wells, J. Catal. 4 (1965) 211.

[33] H.R. Aduriz, P. Bodnariuk, M. Dennehy, C.E. Gigola, Appl. Catal. 58 (1990) 227.

[34] A.N.R. Bos, K.R. Westerterp, Chem. Eng. Process. 32 (1993) 1.

[35] A. Sarkany, A. Horvath, A. Beck, Applied Catalysis A: General 229 (2002) 117.

[36] D. Duca, F. Frusteri, A. Parmaliana, G. Deganello, Appl. Catal. A-Gen. 146 (1996) 269.