Supported carbon nanofibers for the fixed-bed synthesis of styrene [#]

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The styrene synthesis is one of the ten largest industrial processes. This monomer is involved in several polymer syntheses, and is industrially produced by the direct dehydrogenation of ethylbenzene at 873–953 K over a potassium promoted iron oxide catalyst [1]. This strongly endothermic process suffers from drawbacks such as thermodynamic limitations, a large amount of wasted energy, an irreversible catalyst deactivation and coke deposition [2]. Among the alternative technologies developed, the exothermic and non-thermodynamically-limited oxidative dehydrogenation (ODH) of ethylbenzene is promising. Carbon is reported to be catalytically active for the reaction [3,4]. It has been shown that high performances could be obtained over onion-like carbons and carbon nanotubes [5–8], such non-planar sp^2-nanocarbons being very active and promising alternative catalysts to the industrial catalyst, with a higher styrene yield and a lower reaction temperature. The nanocarbons also remained more stable against combustion in an oxidative atmosphere than active carbon [7,8]. A redox mechanism at the carbon surface has been put forward [4–9], involving the oxygen activation on metallic basal planes and the ethylbenzene dehydrogenation on nucleophilic Bronsted basic –C=O groups at the edge/kink sites [6,7].

However, the powdery primary form of such nanocarbons is highly detrimental to a use in fixed-bed reactors for industrial applications. They are prone to block fixedbed reactors, resulting in pressure drops, and leading to moving-bed phenomena; they are excessively difficult to handle and their suprastructural properties cannot be controlled. Since post-synthesis shaping by compaction changes the chemical properties of the nanocarbon materials and inhibits diffusion of reactants and products inside the compacted material, we gave a macroscopic design to the nanocarbons, by anchoring them onto a macroscopic carbon felt support with an open structure. The carbon felt maintains the continuity of chemical properties with the nanocarbons, and shows a higher resistance towards combustion than active carbon and a higher thermal conductivity than alumina, being thus a stable support that can also prevent the appearance of hot spots during the exothermic ODH reaction.

Immobilized carbon nanofibers were obtained following the process described in Ref. [10], by catalytic chemical vapor decomposition of a mixture of ethane and hydrogen (1:5) at 700° C over metallic nickel (1 wt.%) supported on the non-porous carbon felt (surface area < 1 m2/g—Carbone Lorraine). Detailed synthesis and characterization can be found elsewhere [10]. A growth for 2 h led to a weight increase of 100 wt.%, with an increase in the surface area of the

material to 100 m2/g. The high external surface area of the composite results from the prismatic planes exposed at the outer surface of the nanofibers. The carbon atoms at the edge sites are more reactive than atoms located in the interior of the graphene sheets, and the surface exposed by the carbon nanofibers was thus decorated by oxygenated groups [11]. Each supporting fiber was coated by a network of chinese-hat 40 nm diameter carbon nanofibers, with a large void volume between each fiber and each nanofiber (Fig. 1). The composite was directly used as catalyst (i) without any post-synthesis shaping and using no binders, (ii) without any purification treatments, due to a high purity resulting from a total selectivity to nanofibers and the high nanofiber yield.
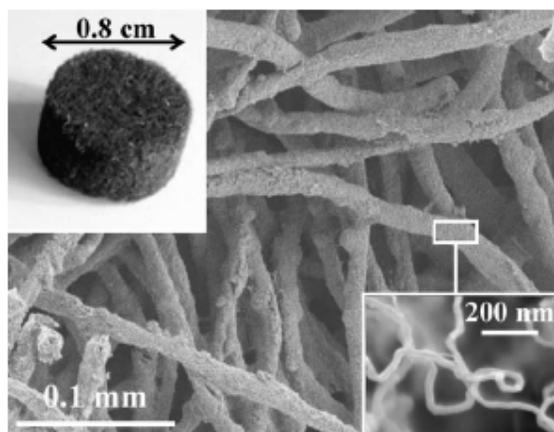

Fig. 1. Optical appearance and SEM image of the nanocarbon composite catalyst.

The felt supported carbon nanofiber composite is an active and selective catalyst even at low temperatures (2 vol.% ethylbenzene, 2 vol.% oxygen, balance helium) and combines the properties of the nanocarbons and the advantages of the macrostructured felt support. Table 1 shows their performances as a function of time on stream at 425° C and 515° C at a flow rate of 30 ml min^{-1}. Similarly to powdery sp^2-bound nanocarbons [6,7], the macroscopic nanocarbons were stable with time on stream in severe conditions, i.e. a large excess oxygen and the high temperature of 515° C. This differed from lamp black carbon, which burnt off and deactivated on stream, being totally combusted after 12 h on stream [8].

Table 1
Conversion of ethylbenzene, selectivity and yield to styrene for different durations on stream

Time (h)	Ethylbenzene conversion (%)		Styrene selectivity (%)		Styrene yield (%)	
	425° C	515° C	425° C	515° C	425°C	515°C
5	–	28.5	–	79.4	–	22.7
8	19.8	28.0	86.7	80.3	17.2	22.5
15	19.1	27.5	88.0	78.4	17.3	21.5
[a]	19.0	28.9	89.0	80.5	16.9	23.3

The total flow rate was 30 ml min^{-1}.
[a] Values after several cycles of increasing/decreasing temperatures.

Fig. 2 shows the performances obtained at temperatures ranging from 375° C to 530° C for total flows of 30 ml min^{-1} and 8 ml min^{-1}. Under both conditions, increasing the temperature led to a slight decrease in the styrene selectivity, the carbon balance was mainly closed by CO_2. The selectivity was not strongly influenced by the space velocity, with a 2–5% range increase when increasing the flow, depending on the temperature. By contrast, the space velocity strongly influenced the ethylbenzene conversion, especially for low temperatures for which an absolute

gain in conversion of 25% was observed. For both space velocities, the maximum of performances in terms of conversion and styrene yield was dependent on the flow and shifted from 492° C to 440° C when the flow was decreased (Fig. 2 inset). At a 30 ml min^{-1} flow, the catalyst showed a maximum of styrene yield of 25% at a temperature of 492° C, with a selectivity to styrene of 81% whereas the yield increased to 38% at 440° C with a similar styrene selectivity at a flow of 8 ml min^{-1} (see Fig. 3). Comparison with the literature is rather difficult since the nanocarbon performances are directly related to their microstructure, which strongly differs from a nanocarbon to others [6–8]. The porosity of activated carbons also seems to play a negative role by hindering the styrene desorption and favouring non-selective consecutive reactions by artificially increasing the residence time of molecules inside the catalyst [4]. By contrast, the open structure of non-porous macroscopic nanocarbons avoided the material compaction during the test and strongly reduced such non-selective consecutive reactions, allowing high styrene selectivity to be obtained compared to bulk nanocarbons [8].
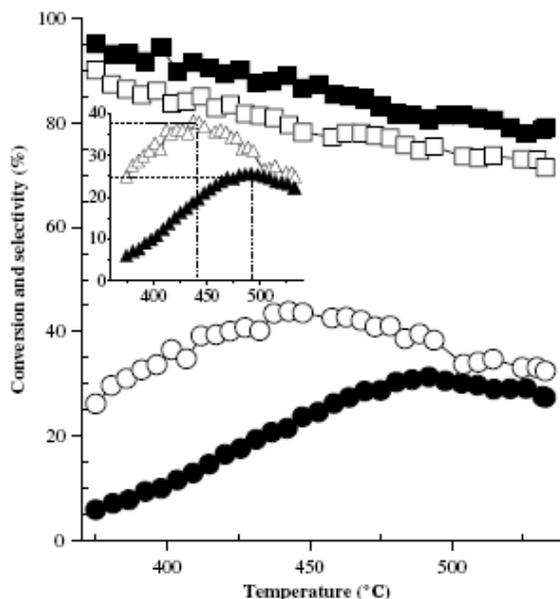

Fig. 2. Ethylbenzene conversions ○, ●) and selectivity to styrene (□, ■) on the macroscopic carbon nanofibers as a function of the reaction temperature in the range 375–530° C, using a total flow rate of 30 ml min^{-1} (full symbols) and 8 ml min^{-1} (empty symbols) respectively. The inset figure shows the resulting styrene yield (△, ▲) for both flow rates as a function of the temperature.

No oxygen remained in the stream for temperatures higher than that of maximum yield, together with a decrease in the styrene selectivity by the ethylbenzene total oxidation with increasing temperature. The ethylbenzene combustion being more oxygen-demanding than the styrene production, the conversion decreased when part of the oxygen is consumed by total oxidation due to the limited oxygen supply.

Decreasing the space velocity led to a higher ethylbenzene conversion for a given selectivity at a lower temperature. This implies that operating by combining a low temperature (440° C) and a low space velocity results in high styrene yields (38%) with a styrene selectivity (81%) that could make such supported carbon nanofibers attractive for industrial applications, a low flow favouring reactant adsorption and a low temperature minimizing the combustion. Whatever the reaction conditions, and in particular the space velocity, no pressure drop occurred in the reactor and the catalyst bed. This strongly differed from the high pressure drop observed at similar reaction conditions using nanocarbon powders. The control of the pressure in the catalyst bed is attributed to the open structure of the macroscopic carbon nanofibers. A large void volume remained available between each supporting fibers and the carbon nanofibers themselves, avoiding the restricting problems related to fixed-bed applications of nanomaterial catalysts and

rendering the whole external surface of carbon nanofibers available for the reactant adsorption. The nanocarbon composite contains 50 wt.% of inactive very low surface area fibers, with a very low density of sites for oxygen activation and of oxygenated sites for ethylbenzene dehydrogenation. The activity is thus due to the 50 wt.% of immobilized high external surface area nanofibers.
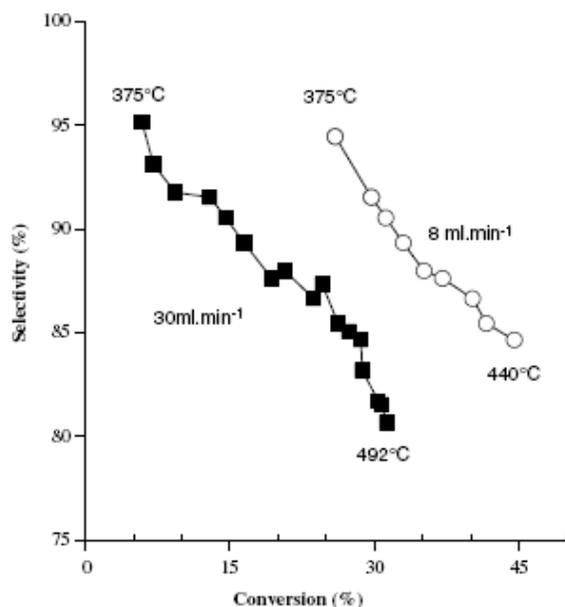

Fig. 3. Ethylbenzene conversion–styrene selectivity plot on the macroscopic carbon nanofibers at total flow rates of 30 ml min^{-1} (■) and 8 ml min^{-1} (○).

Transferring the performances of nanocarbon powders to nanocarbons assembled to a macroscopic shape avoids drawbacks of a powdery primary form and opens routes for designing catalysts for oxydehydrogenation reactions involving hydrocarbons as a general alternative to endothermic thermodynamically-limited direct dehydrogenation reactions.

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