

# Nanocarbons as High Performance Catalysts for the Oxidative Dehydrogenation of Ethylbenzene to Styrene

D.S. Su<sup>1</sup>, N. Maksimova<sup>1</sup>, N. Keller<sup>2</sup>, G. Mestl<sup>3</sup>, M.J. Ledoux<sup>2</sup>, R. Schlögl<sup>1\*</sup>

1: Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany

2: Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), UMR 7515 CNRS, Louis Pasteur University, 25 rue Becquerel BP 08, F-67087 Strasbourg Cedex, France

3: NanoScape AG, Frankfurter Ring 193 a, D-80807 München, Germany

Carbon and its applications are an old subject in heterogenous catalysis. Porous carbons, and especially active carbon, are usually widely used as catalyst supports in a variety of reactions. However, only few works have reported the use of nanocarbon as potential industrial catalysts [1,2]. In the present work, we report on the first application of carbon nanotubes and related materials in the oxidative dehydrogenation of ethylbenzene (ODH) to styrene [3]. The production of styrene monomer from ethylbenzene is one of the ten largest production processes in the chemical industry with an annual styrene production of 23 million tons and mainly performed via the direct dehydrogenation of ethylbenzene. Because this process is endothermic and energy-consuming there is a strong incentive for the development of alternative technologies. ODH is promising due to the realization of an exothermic reaction, but such a process requires an active and selective oxidation stable catalyst.

We have tested a large variety of  $sp^2$  nanocarbons for the ODH of ethylbenzene to styrene at temperatures between 450°C and 550°C [3]. The following  $sp^2$  nanocarbons are used:

- Commercially available multi-walled carbon nanofilaments (CNFS) produced by catalytic hydrocarbon decomposition supplied by Science Inc.
- Bamboo-like nanofilaments (BNFs) prepared by decomposing hydrocarbons over iron nanoparticles embedded in silica by thermal CVD at 1023 K and 600 Torr, supplied by Nanolab Boston (USA).
- Multi-walled carbon nanotubes (MWNTs) obtained via catalytic decomposition of ethane supplied by the LMSPC (Strasbourg).
- Multi-walled carbon nanotubes (MWNTs-A) synthesized using the arc-discharge graphite evaporation technique supplied by the Institute of Catalysis (Novosibirsk).
- Onion-like carbon (OLC) prepared from ultra-dispersed diamond by thermal treatment at 2143 K.

Ethylbenzene was evaporated at 35°C and fed with a He flow (total flow 10 ml/min) to the quartz tube reactor (4 mm i.d. x 200 mm) holding 0.02 g of catalyst particles between two quartz wool plugs in the isothermal zone. The products were analysed by an on-line gas chromatograph equipped with two columns for simultaneous analysis of aromatics and permanent gases. The ODH was conducted with a Weight Hourly Space Velocity of 3 h<sup>-1</sup> (relatively to ethylbenzene) and an O<sub>2</sub>/ethylbenzene molar ratio of 1:1. The catalytic performances of the tested nanocarbons at 550°C are summarized in Fig. 1 in terms of styrene yields.

0 \_\_\_\_\_

\* The work was carried out in the frame of European Laboratory of Catalysis and Surface Science (ELCASS)

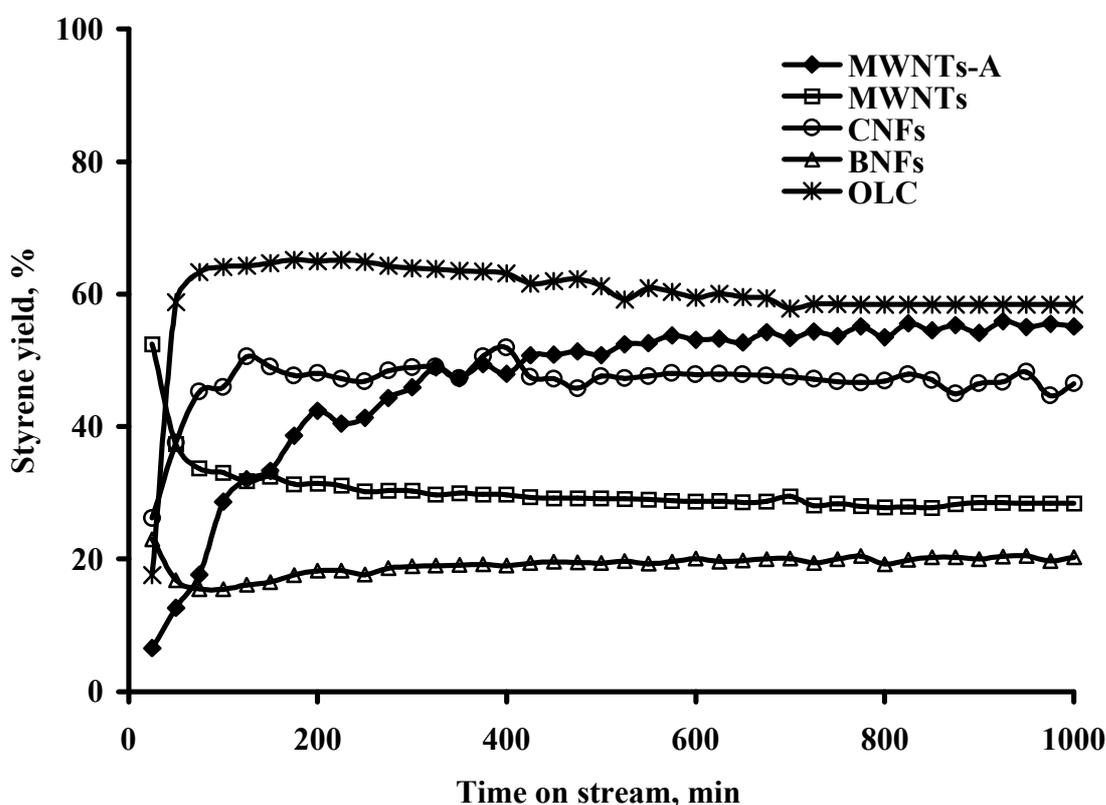


Fig. 1 Styrene yields as a function of time on stream obtained over MWNTs-A, MWNTs, CNFs, BNFs, and OLC in the ODH of ethylbenzene.

All results obtained confirm that carbon in non-planar graphitic form catalyses the ODH of ethylbenzene with high activity and selectivity. The styrene yields using MWNTs and BNFs as catalysts decrease at the beginning of the reaction, but remain nearly constant after 250 min. OLC and CNFs need a short induction period before the styrene conversion reaches an equilibrium state. MWNTs-A needs a longer induction time when compared to OLC and CNFs. The catalytic activity only shows a minor dependence on the  $O_2$  concentration under the reaction conditions, i.e., the reaction seems to be of 0<sup>th</sup> order with respect to oxygen within the  $O_2$  to ethylbenzene molar ratios from 0.5 to 2.5. The results of the kinetic experiments support the working hypothesis of a Langmuir-Hinshelwood mechanism including dehydrogenation steps followed by the oxidation of hydrogen released from ethylbenzene molecules to water. Structural investigation reveals that the activity and selectivity of the  $sp^2$  carbon is related to the optimised distribution of sites required for the oxygen activation (basal planes of carbon) and basic centers (specific oxygenated surface groups), where ethylbenzene adsorption takes place. Pre-treatment experiments of OLC and *quasi in-situ* MX-XPS-UPS reveal that carbonyl-quinone and phenol groups are involved in the ODH of ethylbenzene to styrene.

### References

- [1] G. Mestl, N. Maksimova, N. Keller, V.V. Roddatis, R. Schlögl, *Angew. Chem. Int. Ed.* 2001, **40**(11), 2006
- [2] N. Keller, N.I. Maksimova, V.V. Roddatis, M. Schur, G. Mestl, V.L. Kuznetsov, R. Schlögl, *Angew. Chem.* 2001, **41**, 1885
- [3] N. Maksimova, N. Keller, G. Mestl, D. S. Su, R. Schlögl, submitted to *J. of Catalysis*.