

Nanocarbon materials for the styrene synthesis: on active surface groups and reaction mechanism.

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Styrene (ST) is industrially produced by the direct dehydrogenation (DH) of ethylbenzene (EB) accounting for more than 90 % of the worldwide capacity.^[1] This strongly endothermic process is industrially carried out at high temperatures over a potassium promoted iron oxide catalyst in the presence of a large excess of overheated steam. Detrimental thermodynamic limitations, and large amounts of wasted energy led to the development of alternative processes. Among them, the exothermic oxidative dehydrogenation (ODH) of EB to ST is one of the most elegant and promising reactions due to the absence of equilibrium limitations.^[1] The superiority of non-planar, sp^2 -bound nanostructures such as carbon nanofilaments and onion-like carbons (OLC) as compared to more traditional forms of carbon materials has been reported.^[2,3] The high performance of OLC was related to its microstructure offering a low ratio of prism to basal planes.^[3] The aim of this study was to achieve more insight into the reaction mechanism and the active surface groups of carbon catalysts for ODH. To this end, sp^2 - and sp^3 -bound nanocarbons, OLC and ultra-dispersed diamond (UDD), respectively, are very valuable tools due to their clean and well defined surfaces (Fig. 1).

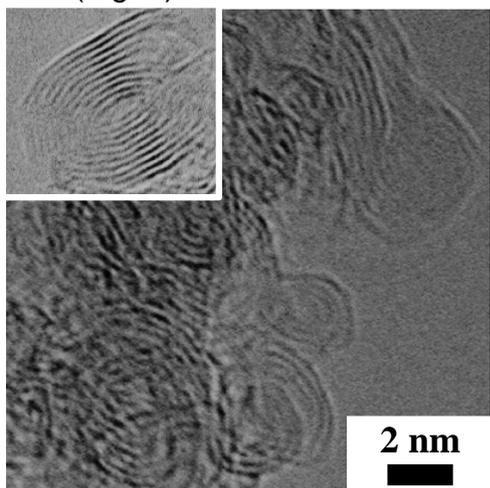
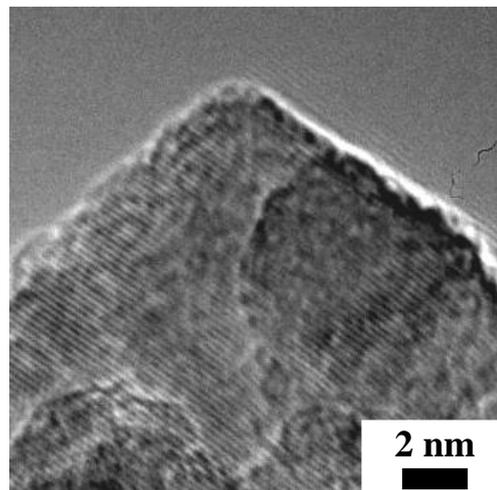


Fig. 1: Onion-Like Carbons (OLC)



Ultra-Dispersed Diamond (UDD)

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Experimental and Results

OLC are produced by graphitization of UDD powder via thermal annealing at 2140 K in vacuum (10^{-6} torr) as described by Kuznetsov et al.^[4] The ODH reaction was performed at 520 °C with a EB/O₂ ratio of 1 and a liquid hourly space velocity of 0,5 h⁻¹.

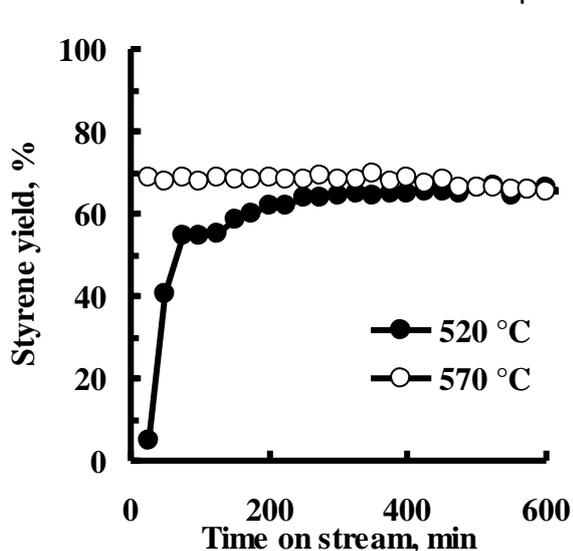


Fig. 2: Influence of the O₂-pretreatment temperature on the ST yield at 520°C over OLC.

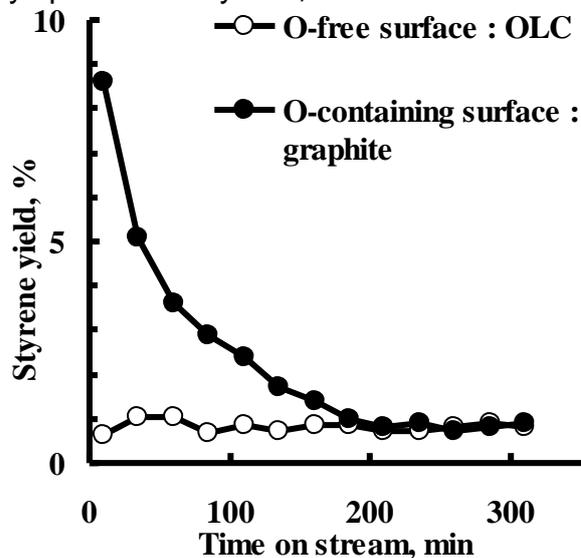


Fig. 3: Influence of the presence of O-surface groups on the ST yield for the anaerobic DH at 520°C.

The possible mechanism for ODH proposed in previous publications distinguished between the dehydrogenating power of basic carbonyl functions and the role of oxygen which is required to regenerate these active centers on the carbon surface.^[3] The influence of different pretreatments of the nanocarbons on the catalyst activation behaviour (Fig. 2) on one side, and the presence of oxygenated surface groups during anaerobic catalytic tests on the other (Fig. 3) allows more insight into the nature of the active centers and the ODH mechanism over sp^2 -carbon structures. Accordingly, both, the presence of strongly basic surface oxygen groups and of gas phase oxygen is required for high activity and selectivity to styrene. Moreover, sp^2 -structures are absolutely required, since sp^3 -UDD initially produced benzene instead of styrene, before UDD was covered by a layer of disordered sp^2 -carbon which in turn led to styrene formation.

High resolution transmission electron microscopy, thermogravimetric analysis, X-ray photoelectron as well as Raman spectroscopies are used to correlate the catalytic behaviours of both sp^2 - and sp^3 -carbon nanostructures and the reaction mechanism to the physico-chemical nature of the surface of the carbon catalysts.

References

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