

CARBON NANOTUBES IN SELECTIVE OXIDATIVE DEHYDROGENATION REACTION

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Carbon nanotubes have attracted a lot of scientific interests nowadays world-wide. The fundamental research works are concentrated in two respects: the synthesis of carbon nanotubes in an economic way for large amount and the application of carbon nanotubes in technology, for instance as new field emitter or for hydrogen storage. Only few works are reported on the use of carbon nanotube as potential industrial catalysts [1]. In the present work, we report on the first application of carbon nanotubes as catalyst in the dehydrogenation of ethylbenzene to styrene [2]. The production of styrene monomer from ethylbenzene is with an annual styrene production of 23 million tons, one of the ten largest production processes in the chemical industry. Because this process is endothermic and energy intensive there is a strong incentive for the development of alternative technologies. The oxidative dehydrogenation is promising due to the realization of an exothermic reaction, but such a process requires an active, selective and stable oxidation catalyst.

We have investigated the catalytic activity of carbon nanotubes for the anaerobic dehydrogenation and oxidative dehydrogenation (ODH) of ethylbenzene to styrene at temperatures between 450 and 550°C [2]. Commercially available purified multi-walled carbon nanotubes with a mean outer diameter of about 100 nm, obtained by the decomposition of ethylene over an Fe catalyst (Applied Science Inc.) are used. For comparison, carbon black (Lamp soot of Degussa) and commercial graphite have been also tested as a catalysts for the ODH of ethylbenzene in similar experimental conditions.

Ethylbenzene was evaporated at 35°C and fed with a He flow (total flow 10 ml/min) to a 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 aromatic and permanent gases. The ODH was conducted under the same conditions with addition of oxygen in the stoichiometric ratio to EB of 1:1, at a Weight Hourly Space Velocity of 3 h⁻¹ (relative to ethylbenzene). The characterization of the carbon nanotubes before and after

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the catalytic tests was done by transmission electron microscopy, thermogravimetry and BET surface area analysis.

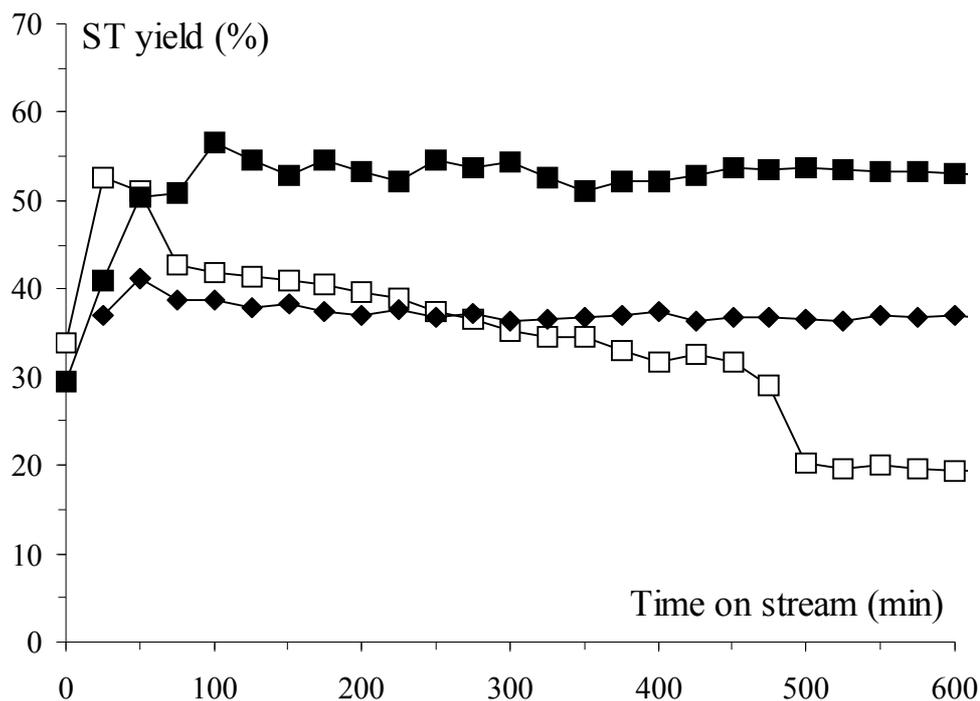


Figure1: Styrene yield obtained with carbon black (□), graphite (◆) and carbon nanotubes ($\phi=15$ nm, ■), evidencing the high performances and the stability of the carbon nanotube catalyst as a function of time on stream.

Figure 1 displays the catalytic performances obtained on the investigated carbon materials with time on stream. The higher activity of nanocarbon relative to soot and graphite is evident. While the catalytic activity of soot decreases during the induction period because of burn-off, that of graphite and the nanofilaments increases or remains stable with time. This behaviour can be correlated with the stability toward combustion [2]. Our results reveal that carbon nanotubes is highly active in the ODH of ethylbenzene to styrene, exhibiting a higher styrene yield relative to graphite and much higher performances than the anaerobic dehydrogenation show. Our investigation opens a new field of applications for carbon nanotubes into the heterogenous catalysis.

References

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