

Reaction Optimization of Oxidative Dehydrogenation of Ethylbenzene to Styrene over Carbon Nanofilaments

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Introduction and aim

The production of the styrene (ST) monomer from ethylbenzene (EB) is one of the ten largest processes of the chemical industry. This industrial process utilizes catalytic, thermal dehydrogenation, despite being highly endothermic and limiting the EB conversion due to thermodynamics. The oxidative dehydrogenation (ODH) of EB seems to be the most promising alternative to the conventional dehydrogenation. This reaction is not thermodynamically limited and slightly exothermic, which reduces the amount of heat that has to be transferred from the reactor. However, such a process requires a suitable active, selective, and stable oxidation catalyst [1].

In previous studies, we found that carbon nanofilaments are selective and stable catalysts in the ODH of EB to ST [2]. This work aimed at optimizing the conversion rate of EB and selectivity of ST by varying the oxygen (O) to ethylbenzene- ratio, reaction temperature, residence time, and EB concentration. To evaluate the use of air as an oxidant, the stability of the samples at high O: EB- ratios was studied.

Experimental

Commercially available multi-walled carbon nanotubes (MWCNT) supplied by Applied Science Inc. were used in the present study. Ethylbenzene was dosed applying a saturator at 35°C and fed after mixing with oxygen and He to a quartz tube reactor (4 mm i.d. x 200 mm) containing 0.01-0.2 g of catalyst particles between two quartz wool plugs in its isothermal zone. The products were analysed by an one-line GC (Varian 8000) equipped with two columns for the simultaneous analysis of aromatics and permanent gases. The microstructure and the surface functionality of the catalysts before and after reaction were monitored by means of TEM, SEM, XPS, and TG-MS.

Results and discussion

As shown in Fig. 1, in the ODH of EB at 425 °C the EB conversion increases with increasing O: EB ratio whereas the ST selectivity decreases. An increase of the number of functional groups on the surface of carbon filaments is assumed to be the reason of the observed enhanced activity. Higher concentrations of CO and CO₂ in the reaction gases indicate that over-stoichiometric O: EB ratios favour the total oxidation of the EB. The highest yield of styrene is obtained at an O: EB ratio of 5. An increase of the styrene yield can also be obtained when we the reaction temperature is somewhat increased.

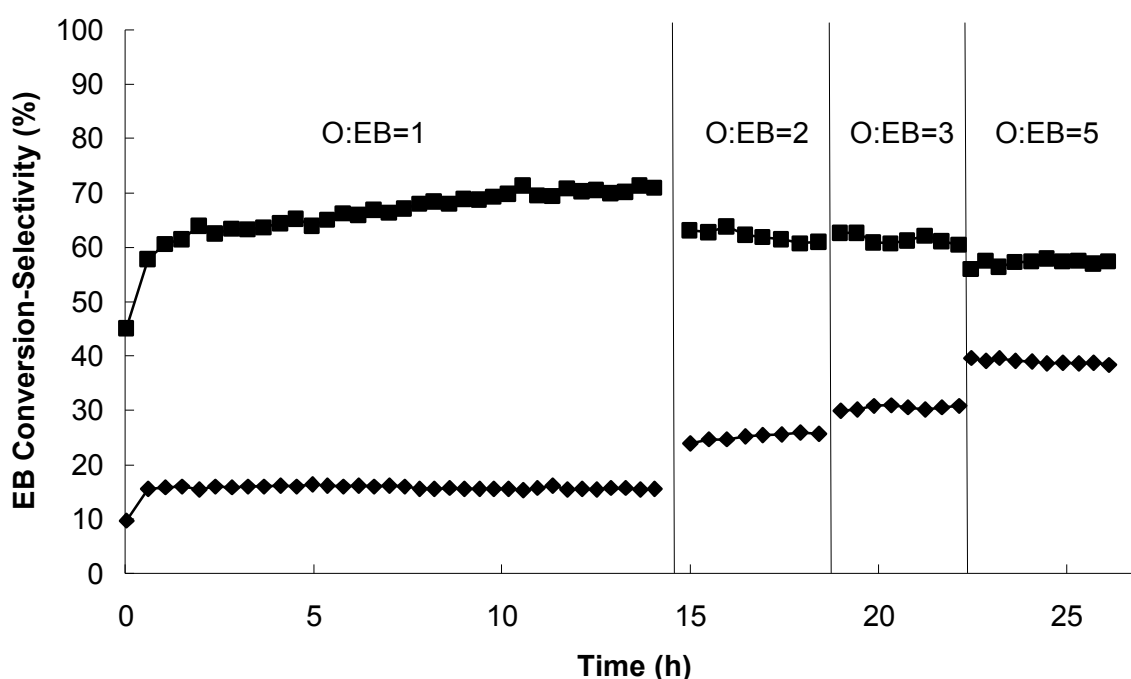


Fig. 1. EB conversion (◆) and ST selectivity (■) of the CNTMW sample at 425 °C at various O: EB ratios.

TEM images of the fresh MWCNT samples exhibited the typical MWCNT structure with edges, which are thought to act as the active sites. A comparison with the images of the used samples did not reveal structural changes. Carbon deposition was neither observed on both, the basal planes nor the edge sites.

Further work is in progress to find improved catalysts and reaction conditions.

1. F. Cavani and F. Trifiro, *Appl. Catal. A: General*, 133 (1995) 219
2. G. Mestl, N. Maksimova, N. Keller, V. Roddatis, R. Schlögl, *Angew. Chem. Int. Ed.* 2001, **40**, No.11, 2006