



Catalysed ethylbenzene dehydrogenation in CO₂ or N₂—Carbon deposits as the active phase

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ABSTRACT

Bare alumina support transforms into an active catalyst for the dehydrogenation of ethylbenzene to styrene in CO₂ or N₂. During the first 15 h time on stream in CO₂, or the first 10 h time on stream in N₂, the alumina shows an increase in ethylbenzene conversion and styrene selectivity from 15% to 60% and from 60% to 92%, respectively, under industrially relevant conditions of 600 °C and 10 vol% ethylbenzene. Thereafter, the system slowly deactivates, but remains highly selective. TGA analysis shows an increase in coke content. The specific surface area and pore volume show a decrease with time on stream. TEM-imaging reveals that the spent catalyst surface is completely covered by several layers of coke. These results combined suggest that the carbon deposits on the alumina are responsible for the increase in activity and selectivity, and also are the cause of deactivation once a monolayer of carbon is deposited on the support surface. Similar trends are observed for zirconia support. Supported vanadium and chromium oxides on alumina all give similar results, but after a faster activity development. Also for these supported catalysts and even carbon samples, deposited coke is the active and selective phase.

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1. Introduction

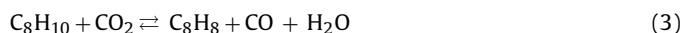
Styrene monomer is one of the largest bulk monomers at this moment and will probably be in this position for a long time to come. In industry it is mainly produced by steam-aided dehydrogenation of ethylbenzene over a promoted potassium-iron catalyst. This process suffers from high energy requirements and low per-pass conversions due to its endothermic nature and equilibrium limitations. A large part of the energy is lost in the steam condensation, which cannot be recovered due to practical reasons [1,2].

To overcome these issues, oxidative dehydrogenation with pure oxygen has been explored. This solves the issues related to the endothermic nature of dehydrogenation and its equilibrium limitations, but brings its own issues. It has a poor selectivity due to secondary oxidation, safety issues like risk of explosion, and may lead to hot-spots in the catalyst bed due to the highly exothermic nature of this type of reaction. Due to these issues and the higher operating costs oxidative dehydrogenation has not been commercialised yet [2].

CO₂ has been investigated as an alternative oxidant for this process. The use of CO₂ is safer than using oxygen and at the used

temperatures CO₂ is considered to be a mild oxidant that relaxes the equilibrium limitations of the current steam-aided dehydrogenation process. Also the energy losses due to steam condensation can be circumvented, making the overall process energy saving [3–7].

The CO₂ oxidative dehydrogenation (ODH) process is, however, still equilibrium limited [4]. The equilibrium conversion at 600 °C and 1:10 ratio of EB:CO₂ is 91%, compared to 76% for the steam-aided dehydrogenation process under the same conditions. The CO₂ oxidative dehydrogenation reaction (3) is a result of a two-step mechanism consisting of direct dehydrogenation (1) followed by the reverse water-gas-shift (RWGS) (2) that removes the hydrogen [4,8].



A lot of research effort has already been put into the development of a CO₂ ODH process for styrene production. Many catalysts have been tested, using many types of supports, and quite active and selective catalysts have been claimed [4–7,9–35]. An often used catalyst support is alumina [6,7,12–17]. The overview in Table 1 shows some examples of alumina supported catalysts with chromium or vanadium. Most of the recent publications on alumina supported catalysts reported that the alumina support itself had a

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