Summary

Styrene (ST) is industrially produced by the direct dehydrogenation of ethylbenzene (EB) using steam at 580-630 °C. The process suffers from high energy consumption and low conversion per pass because of equilibrium limitations even at the high temperatures required for the endothermic reaction. As such, there is an ongoing effort to identify improved styrene production processes. An example is the oxidative dehydrogenation process, which has the advantage that i) it can be operated at considerably lower temperatures, ii) there is no need for co-feeding of superheated steam and iii) high conversions per pass can be attained as thermodynamic limitations are absent. However, commercial operation has not been realised yet and considerable research and development activities are required in the field of heterogeneous catalysis engineering.

The general aim of the research described in this thesis is to develop improved heterogeneous catalysts based on commercial supports such as aluminas, silicas, alumina-silicas, zeolites, and carbon-based materials for the oxidative dehydrogenation of ethylbenzene to styrene under industrially relevant conditions. The main purpose is to improve styrene selectivity and stability, and to establish structure-performance relationships. Regarding selectivity, the catalyst should show at least comparable selectivity to direct dehydrogenation catalysts (i.e. >95%). This is especially relevant when COx is formed during the reaction, which is highly undesirable regarding process economics and environmental aspects. When considering conversion, a conversion higher than the conventional process (60-65%) is aimed for and it is preferentially at least similar to the SMART™ process (i.e. 80%). To achieve these goals, primary and secondary high throughput catalyst screening studies have been performed involving catalysts based on bare commercial carriers, metal-based counterparts, carbon-based materials (commercial and tailor-made), and P-based catalysts.

In Chapter 1 an overview of styrene production processes is presented. Examples include the Lummus/UOP classic styrene technology, the Badger/ATOFINA process, the SNOW process, oxidative dehydrogenation (ODH), and their advantages and disadvantages are discussed. The ODH process is discussed in detail. Various process-related aspects (i.e. selectivity, O2:EB ratio, stability, and space velocity) for the ODH process are described and evaluated.
In **Chapter 2** the positive impact of the thermal activation of a silica-stabilized γ-alumina catalyst for the oxidative dehydrogenation of ethylbenzene to styrene is discussed. A systematic study in a 6-flow set-up reveals that the transition from γ-alumina into transitional phases at 1050 °C leads to an increase in both conversion and selectivity under pseudo-steady state conditions. During reaction, an active and selective coke is formed on the aluminas. The increase in EB conversion in the optimal system is related to a higher ST selectivity, which makes more O₂ available for the main ODH reaction. The ST selectivity improvement is due to a reduction in the amount of COₓ formed, likely due to the formation of a less reactive coke.

In **Chapter 3**, a systematic study on reaction stability of relevant carbon-based materials, home-made carbon-silica hybrids, commercial activated carbon, and nanostructured multi-walled carbon nanotubes (MWCNT) as catalysts for the oxidative dehydrogenation of ethylbenzene is provided. A relatively concentrated EB feed (10 vol. % EB), and limited excess of O₂ (O₂:EB=0.6) was used to allow for full oxygen conversion and consequently avoid O₂ in the downstream processing and recycle streams. The temperature was varied between 425-475 °C, which is about 150-200 °C lower than for the commercial steam dehydrogenation process. Among the tested catalysts, MWCNT were the most stable under such demanding conditions, followed by commercial activated carbon and home-made carbon-silica hybrids. Catalyst stability was predicted from the apparent activation energies of the combustion reaction. The apparent activation energy of the carbon combustion was calculated by Ozawa method using a correlation between the peak temperature for a given conversion (at 20% and 80%) and the heating rate.

In **Chapter 4** a strategy to enhance the thermal stability of the home-made carbon-silica hybrids, discussed in the Chapter 3, is proposed. It involves P-addition before the pyrolysis. Phosphorous addition has an inhibiting effect on the carbon combustion. The carbon and P loading have an effect on the textural parameters. The mesopores retain the cylindrical shape with a fraction of micropores for P-promoted hybrid catalysts. The carbon-silica hybrids were tested for the ODH process, and it was shown that the P/C/SiO₂ hybrids are more active and selective at elevated temperatures (450-475 °C) than the MWCNT. At low temperature, this positive effect is negligible. Characterization of the spent catalysts shows that substantial amounts of coke were formed on the P/C/SiO₂. Overcoking during the reaction leads to the pore network restrictions, reduction of pore volume and surface area.
Chapter 5 discusses the feasibility to regenerate MWCNT under mild conditions. The regeneration method is described, and the effect of the regeneration time on the pore volume and surface area is discussed. MWCNT can be regenerated under mild conditions. In order to quantify the regeneration efficiency, the weight loss during the regeneration and reaction conditions has been taken into account. At optimal conditions, 70% of the initial surface area can be recovered and the pore volume in 50%. During the study, it was also found that the specific surface area, for prolonged regeneration times, can be even higher than the starting material. This was explained by the cleaning effect of the as-received MWCNT from amorphous domains, at the expense of weight loss.

In Chapter 6 the effect of phosphorous addition to the various inorganic supports was studied. Phosphorous is known to be an active/selective promoter for the ODH reaction. However, systematic investigations regarding the performance (conversion, selectivity) and stability under industrially relevant conditions for phosphorous based catalysts have not been reported to date. In this chapter, the performance of various bare supports (silicas, alumino-silicate, zeolites, and zeolites with low alumina content) and the corresponding phosphorous-based catalysts is investigated. Preliminary characterization of the fresh, spent and regenerated catalysts is presented. A positive effect of phosphorous addition to various supports was shown for the ODH reaction. The most active and selective catalysts were identified and valuable clues regarding future studies on phosphorous addition are presented.