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Oxidative dehydrogenation of ethylbenzene under industrially relevant conditions

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Chapter 1

Introduction

Styrene (ST) is industrially produced by direct dehydrogenation of ethylbenzene (EB) using steam at 580-630 °C. The process suffers from high energy consumption due to low conversion per pass because of equilibrium limitations and the high temperatures required for the endothermic reaction. However, many research groups and companies have investigated alternative styrene production processes. Oxidative dehydrogenation process is one of the most important ones. The big advantage of oxidative dehydrogenation is that the process can be operated at lower temperatures. There is no need for the co-feeding of superheated steam, and it is free of thermodynamic limitations regarding the conversion of ethylbenzene. Thus, high conversion per pass can be achieved. However, various pitfalls in the oxidative dehydrogenation of ethylbenzene to styrene still exist. These aspects are discussed as well as alternative dehydrogenation processes, economic and environmental aspects of styrene production and the thermodynamics of the styrene chemistry.

1.1 Economic and environmental scope of styrene product

Styrene is one of the most important monomer for the polymer industry. Commercial production started in the 1930th on small scale. In 2010 the total annual production of styrene made 26.4 million metric tonnes [1], that makes the industrial dehydrogenation of ethylbenzene one of the most important industrial processes [2-4]. The expected consumption of styrene in 2020 is estimated to be increased to 41 million metric tonnes worldwide [5]. The market price of styrene in Western Europe is about 1550 \$/tonne based on the data of December 2012 [6]. It makes it evident that the total market size of styrene worldwide is immense (\$30-\$50 billion).

An estimated energy consumptions of 6.3 GJ/tonne styrene [7]. The worldwide energy consumption of the styrene production process by dehydrogenation with an annual production of 26.4 million tonnes can be estimated at 1.7×10^{17} J/year (170 PJ/year). This means that an energy efficient production process would be developed, the total worldwide energy consumption and, therefore, the emission of greenhouse gasses could be considerably reduced. This means that both from an economical and environmental point of view, a reduction of the energy consumption of the styrene production process is of great interest.

1.2 Styrene

Styrene is a colorless oily liquid with a sweet smell. It is an aromatic olefin (Figure 1) which is easy can be polymerized due to the presence of carbon double bond. Styrene is named after 'styrax', the resin from the oriental sweet gum tree, native in the eastern Mediterranean region. An overview of some physical properties of styrene is given in the Table 1.

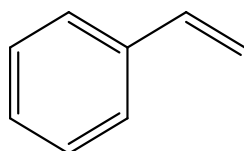


Figure 1. Structure of styrene molecule

Table 1. Physical properties of styrene [8].

Molecular weight [g/mol]	104.152
Density [kg/m ³]	903
Melting point [°C]	-30.6
Boiling point [°C]	145.2
Critical temperature [°C]	373
Critical pressure [atm]	46.1
Viscosity (20°C) [cP]	0.762
Flash point [°C]	31

1.2.1 Styrene monomer uses

According to the "Styrene Producers Association" [9] the main purpose of the styrene is the production of polystyrene (62%) and acrylonitrile-butadiene-styrene (ABS) resins (14%). All main applications are given in Figure 2.

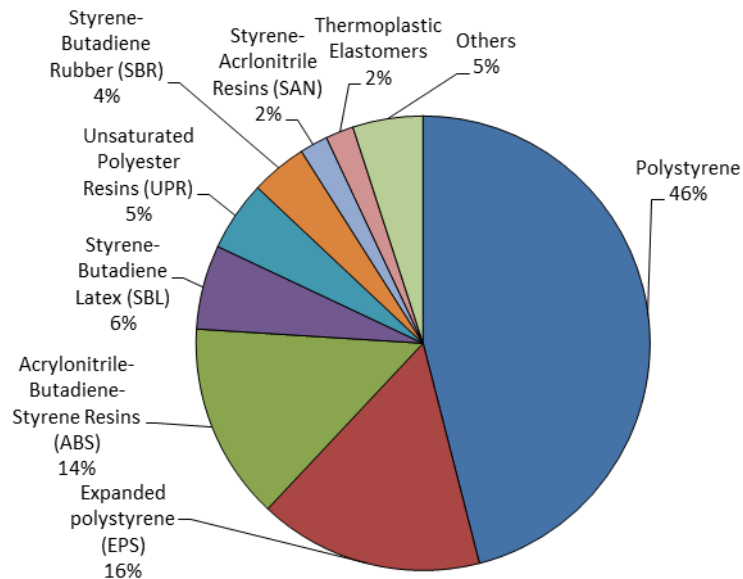
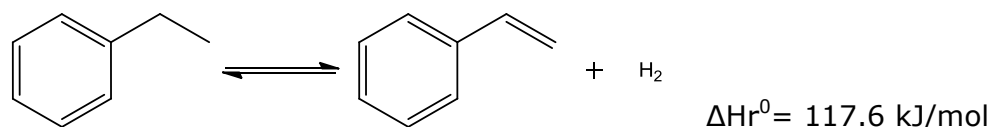


Figure 2. Global demand for styrene monomer derivatives in 2004 [9]. (Reproduced with permission) [9]

Styrene is a main monomer block for the polystyrene production. Polystyrene is widely used because it is relatively inexpensive to produce and easy to polymerize and co-polymerize [10]. The main uses of polystyrene are for disposable cups, trays and bowls, packaging, household appliances, consumer goods, and as building and construction material. For products which need more stiffness, ABS resin is often used. Other smaller uses are as a co-polymer in several synthetic rubbers and resins as shown in Figure 2.

1.3 Styrene production chemistry and thermodynamics

Most of the commercial styrene is produced by direct dehydrogenation of ethylbenzene (85-90%). The remaining part (10-15%) is obtained as a by-product in the production process of propylene oxide [10]. Ethylbenzene is dehydrogenated according to the following reaction:



This equilibrium gas-phase catalytic reaction is highly endothermic ($\Delta_r H_{298}^0 = 117.6$ kJ/mol [11,12]) and it performs in the presence of steam. The equilibrium constant is defined by:

$$K_{eq} = \frac{P_{ST} \cdot P_{H_2}}{P_{EB}} \quad (1-1)$$

where:

- K_{eq} - Equilibrium constant [bar]
 P_{ST} - Partial pressure styrene [bar]
 P_{H_2} - Partial pressure hydrogen [bar]
 P_{EB} - Partial pressure ethylbenzene [bar]

Due to the reaction stoichiometry and the fact that the reaction takes place in the gas phase, a high pressure drives the equilibrium towards EB (Le Chatelier's principle [13]). It means that at low pressure, the system adjusts the position of the equilibrium towards the side of the balance with the larger number of reactants in order to resist the effect of the pressure. Therefore, lower pressures favour the conversion to styrene. The low pressure as 0.4 bar are often applied to the system to increase the styrene yield [10].

This makes it clear that lowering the pressure initiate a larger driving force for the reaction, to the side of styrene and hydrogen.

High temperatures also lead the equilibrium to be on the side of styrene. That is why a low pressure and high temperatures are used in the industrial practice of styrene production by direct dehydrogenation. The effect of low pressure and high temperatures on the ethylbenzene equilibrium conversion is shown in the Figure 3.

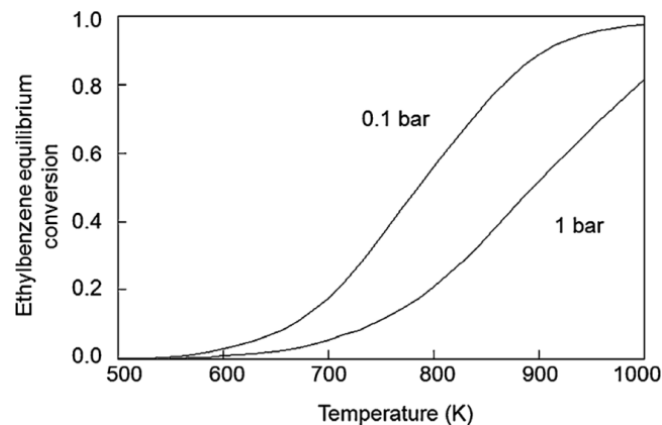


Figure 3. The effect of temperature and pressure on the ethylbenzene equilibrium conversion [14]. (Reproduced with permission)

An excess of superheated steam of 720°C is added with steam:EB molar ratios of 6-13:1 for the styrene production before entering the dehydrogenation reactor. Main reasons are listed below:

- Energy in the form of steam is needed to supply the heat for the reaction [11].
- High temperatures of 550-700°C [2,10,11,15] are needed because the equilibrium constant increases with temperature [10].
- The equilibrium is shifted to higher conversion of ethylbenzene by diluting the reaction system with steam, in order to lower P_{EB} .
- It reduces the formation of unwanted coke deposition on the catalyst particles [2-11].

The use of conventional styrene production by steam dehydrogenation has also several disadvantages:

- High energy consumption due to the use of superheated steam.

- The reaction is equilibrium- and thermodynamically limited at 50- 65%, which requires a large reactant recycle [11,15]
- Separation of EB and ST is difficult due to a similar boiling point of respectively 136 °C and 145°C
- Consumption of feedstock and product by side reactions forming syngas (CO + H₂) [11].

1.4 Styrene production technologies

1.4.1 Lummus/UOP classic styrene technology

The Lummus/UOP Classic SMTM is a major technology for the styrene production. Approximately 43 plants worldwide operate using this technology, with a cumulative production of 8.3 million tonne annually [16]. In the Figure 4 is shown, that for this process the outlet flow of the dehydrogenation section is cooled down, and then it is distilled to separate the different products (styrene, benzene, toluene, and tar); the non-reacted ethylbenzene is recycled.

In the dehydrogenation section, ethylbenzene is dehydrogenated over potassium promoted iron catalyst in an adiabatic fixed bed reactor. More than one reactor is used since the temperatures drop in a theoretical adiabatic reactor under 100% ethylbenzene (theoretical) conversion is $\sim 330^{\circ}\text{C}$ [14] (Figure 4). A temperature drop is undesirable for a good performance of the dehydrogenation reaction.

Lummus/UOP developed a more efficient process for styrene production called the SMART process, which is implemented in several plants worldwide with an annual cumulative production of 1.4 million tonnes. This process is based on the classic styrene monomer process with a difference in the dehydrogenation section (Figure 5). The number of plants using the SMART technology is limited due to the safety risks involving a high temperature mixture of oxygen and hydrogen which presents in the reactor.

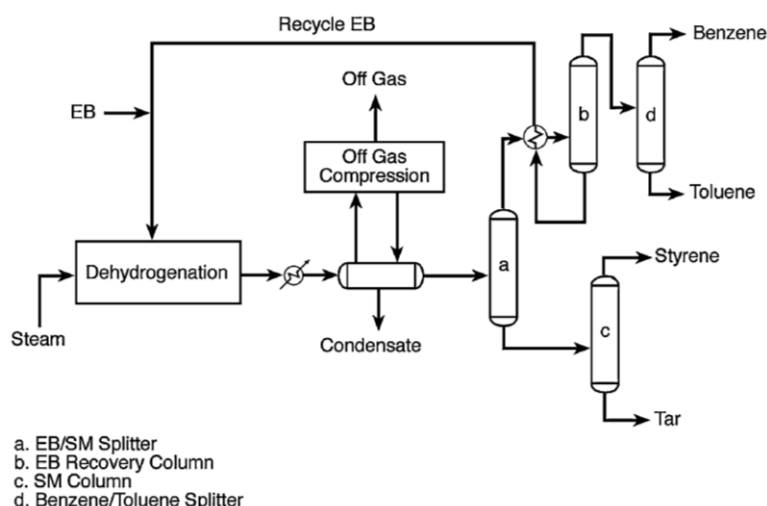


Figure 4. PFD of the Lummus/UOP classic SM process [10]. (Reproduced with permission)

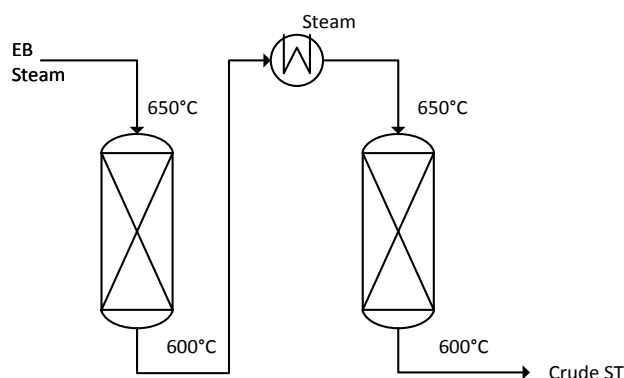


Figure 5. Conventional reactor configuration for the dehydrogenation section of ST production (Steam/EB = 12- 17 mol/mol) [14]. (Reproduced with permission)

The dehydrogenation section of the SMART process contains an extra reactor between the existing dehydrogenation reactors. This extra reactor contains both an ethylbenzene dehydrogenation and a hydrogen oxidation catalyst, as shown in Figure 6. The additional conversion of hydrogen causes the equilibrium to shift towards ethylbenzene, resulting in a higher conversion per pass of up to 75% [16]. The energy release by oxidation is used to decrease the amount of steam used and therefore lowers the energy consumption.

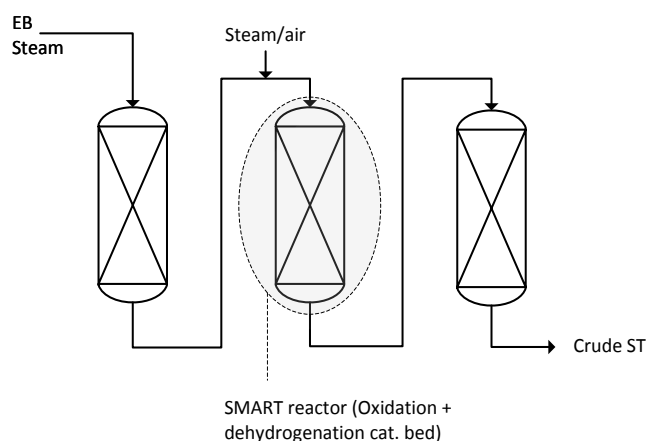


Figure 6. Dehydrogenation section Lummus/UOP SMART™ process [16]. (Reproduced with permission)

1.4.2 Badger/ATOFINA styrene technology

The Badger/ATOFINA process is another major technology for the styrene production, with 47 plants licenced worldwide with a cumulative annual production of 9 million tonnes [16]. This process uses potassium promoted iron catalyst as well [18].

The main difference with the Lummus/UOP process is the distillation section. In the Badger/ATOFINA process benzene and toluene are separated from styrene in the first distillation column downstream of the settling drum (Figure 7, a). In the next column, ethylbenzene and styrene are separated and the remaining

ethylbenzene is mixed with fresh ethylbenzene and it is fed back to the first dehydrogenation reactor. Finally, in the last column styrene is separated from residues. All columns are designed to operate below atmospheric pressures to minimize the operating temperature and to prevent polymer formation [10].

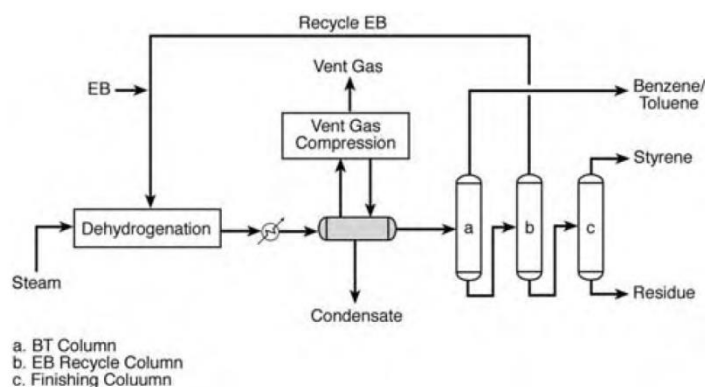


Figure 7. PFD of the Badger/ATOFINA styrene process [10]. (Reproduced with permission)

The dehydrogenation section of this technology is partly different from the Lummus/UOP process. In the Badger/ATOFINA process the dehydrogenation section also includes two packed bed columns with interstage heating of the reaction mixture. It helps to cope with the temperature decrease due to the endothermic nature of the reaction. However, the exit stream of the first reactor in the Badger/ATOFINA process is not injected with steam directly, but is reheated by a heat exchanger (Figure 8).

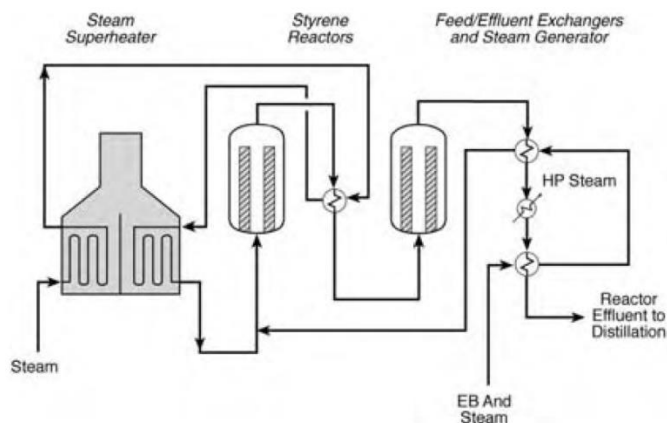


Figure 8. PFD of the Badger/ATOFINA styrene process [10]. (Reproduced with permission)

1.4.3 SNOW process

Since the main purpose of ethylbenzene is the production of styrene, it is produced in the most of cases on site of a styrene production plant by alkylation of benzene with ethylene. Thus, the raw material price is costs of benzene (66%) and ethylene (34%) [10]. In order to reduce the risk of ethylene prices fluctuations, Snamprogetti and Dow (hence SNOW) developed a process that can run on both ethylene and ethane. Furthermore, ethane is often a cheap by-product of petrochemical streams [17], which makes it possible to integrate a styrene plant into a petrochemical plant

without the use of a steam cracking unit to produce ethylene. Moreover, the integration of ethylene- and ethylbenzene production with styrene production possibly can generate a great reduction in capital expenses for the total styrene production process.

A plant running on SNOW technology is fed with benzene and ethane, the latter being dehydrogenated in the same reactor as ethylbenzene, to produce the stoichiometric amount of ethylene for the alkylation of benzene (Figure 9, top). Alternatively, a plant with SNOW technology can run on benzene and ethylene as feedstock, working similarly as the conventional styrene technology described earlier (Figure 9, bottom).

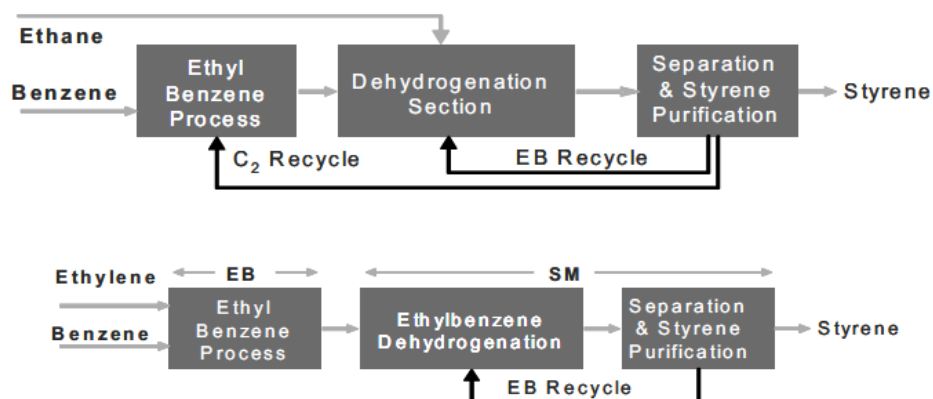


Figure 9. Flow scheme for SNOW technology with the ethane option (top) and the conventional ethylene option (bottom). (Reproduced with permission)

The reactor section of the SNOW process is considerably different to the other direct dehydrogenation processes due to the simultaneous dehydrogenation of ethylbenzene and ethane. The reactor section consists of a riser type reactor in which the gas inlet stream is mixed in co-current with fresh catalyst and moves upwards under gas velocities of 4-20 m/s (Figure 10). The catalytic reactions are performed rapidly (approximately 1-5 seconds) in the riser [17]. The temperature ranges among 590-700°C; it does not run below atmospheric pressures to shift the equilibrium and increase the selectivity in comparison with the more conventional dehydrogenation process. The temperature is supplied by the heat capacity of the catalyst particles [18].

The regeneration of the spent catalysts takes place in a bubbling fluidized bed under air to burn off possible coke formation. Then regenerated catalyst is fed back in the bottom of the riser. The reactor outlet stream is separated and processed using conventional separation technology [17].

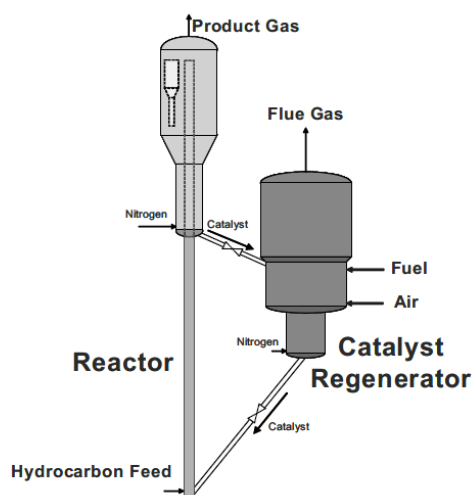
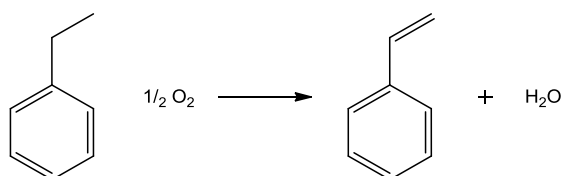


Figure 10. Reactor section of the SNOW process [21]. (Reproduced with permission)

The production process of styrene by direct dehydrogenation is developed to a high degree of maturity, and there is not much can be improved [17]. Also, the price of feedstock greatly determines the profit margin of styrene production, as 80% of the production costs comes from raw material feedstock [10]. The development of the SNOW process responds to this and decreases the raw material cost with approximately 14% [17]. Moreover, it decreases the energy consumption due to the absence of superheated steam using for dilution of the reaction mixture.

1.5 Oxidative dehydrogenation of ethylbenzene

In the oxidative dehydrogenation of ethylbenzene to styrene EB is feed simultaneously with oxygen for the styrene formation according to the following reaction:



In contrast to direct dehydrogenation this reaction is oxidative and, therefore, exothermic ($\Delta H_r^0 = -124.3$ kJ/mol [11,12]). The big advantage of oxidative dehydrogenation is that the process can be operated at lower temperatures. There is no need in the co-feeding of superheated steam, and it is free of thermodynamic limitations regarding the conversion of ethylbenzene [19]. Thus, high conversion per pass can be achieved without using a vacuum.

1.5.1 Nature of the active coke

The ODH of EB has been studied for four decades. In 1973 Alkhozov *et. al.* [20] first proposed that actual catalyst for the ODH is the layer of carbonaceous deposits formed on acidic catalysts as alumina during the first hours of the reaction. This was later confirmed by many authors who studied this phenomenon and became the general conclusion [21-29].

The layer of active coke consists of carbon, oxygen, and hydrogen. The ratio of these species in the molecules of the coke layer varies with the time on stream. It was shown that the C/H ratio increases with the reaction time and varies between 0.5-4 in steady state [23,27,28]. Active coke contents between 5.0-33.7 wt.% have been reported [22-25,28,30-33].

The active coke in the ODH of ethylbenzene is ascribed to redox couples formed on a polycyclic aromatic basis, being the coke molecules. A reaction mechanism based on experiments with zirconium phosphate as a support material was proposed by Emig and Hofmann (Figure 11).

According to this model, coke is formed from the condensation of styrene on the catalyst support material. It has to be noted, that styrene can be present without the availability of active coke because direct dehydrogenation can occur to a small extent [26]. However, later Lisovskii and Aharoni [32] showed that the reactivity's of styrene and ethylbenzene are very similar. The mechanism proposed by Emig and Hofmann is very similar to the reaction mechanism introduced by Iwasawa et al. [21] for the ODH of ethylbenzene over polynaphthoquinone.

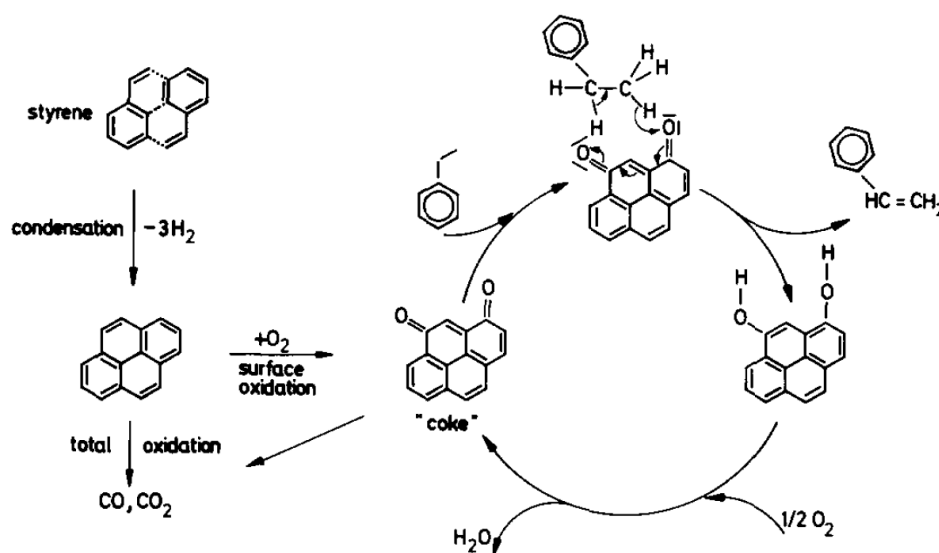


Figure 11. Mechanism for the ODH of EB proposed by Emig and Hofmann [23]. (Reproduced with permission)

In this proposed reaction scheme, styrene is condensed to a system of polycyclic aromatic rings on the catalyst support surface. Afterwards, these rings are oxidized and form the polyquinone structure, which has a name of "coke" in Figure 11. This polyquinone structure oxidizes EB to styrene and reacts to a polyhydroquinone intermediate. Thereafter, the polyhydroquinone structure is oxidized by half molecule of O_2 to polyquinone one more time. Several research groups confirmed that the mechanism demonstrated in Figure 11 is the most probable reaction mechanism [12,25,28,29,32]. Recently, it was shown that carbonyl/quinone groups indeed act as active sites for the ODH reaction. Hence, the activity of the catalyst is directly related to the concentration of the carbonyl groups in the coke layer on the catalyst [34].

Moreover, Lisovskii and Aharoni [32] showed that in the case of interruption of ethylbenzene supply with the constant space velocity, the production of styrene stops immediately. This implies that styrene is not formed out of a carbonaceous intermediate but directly from ethylbenzene, which makes the proposed reaction mechanism in Figure 11 more feasible.

Vrieland showed that the active coke is not the major source of CO_x [23]. It appears that styrene and ethylbenzene react more readily with oxygen than the deposited carbon does. There are indications that the active coke actually catalyses the burning of styrene and ethylbenzene, as the CO_x formation increases with increasing carbon coverage of the support [20,23].

1.5.2 Supports properties for the active coke formation

1.5.2.1 Surface acidity of the support

For the formation of an active coke layer, the support must have some acidity; basic supports as magnesia and titania are almost completely inactive [30]. Coke formation is accelerated by acidic centers [23], but a narrow distribution of acidity is required for obtaining an active and selective coke layer. In general, acidic sites with moderate to low acid strength, give the largest contribution to the formation of catalytically active coke for the styrene production [22,24,25]. In several publications has been stated that the supports with the highest total acidity have the greatest active coke formation [28,36], while other researchers state that very strong acidic site are either ineffective or promote cracking and other side products [22,23]. Although some authors discuss the total acidity of the support (Brønsted and Lewis), moderate Lewis acid strength is considered necessary for the formation of proper coke [29].

1.5.2.2 Textural properties of the support

Textural properties of the support are important factors to achieve good performance. For this reason it is interesting to know the effect of coking on a support as a high rate of coke formation can block the pore mouth of the micropores and sometimes mesopores. Figure 12 illustrates the effect of slow and rapid coking. The former results in an equal distributed layer of coke in the micropores (a), the latter results in pore mouth plugging by the coke (b).

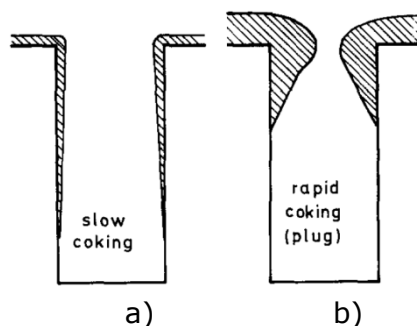


Figure 12. Schematic representation of the coke formation rate [31]. (Reproduced with permission)

Olefins are known to have a large rate of coke formation compared to other hydrocarbons [31]. This corresponds with the reports that catalyst particles with meso- and macro pores show better results in the ODH of ethylbenzene by active carbons than microporous materials, because the micropores are quickly and almost completely blocked by the formed coke [35,36]. These studies used carbon as catalyst, but it shows the influence of the coke on the textural properties. This results of the BET surface area approaching the area of the meso- and macropores also known as 'external surface area'. Furthermore, catalytic behaviour cannot be

directly related to the surface area, which makes it clear that this is not the only essential parameter for the reaction [37]. Hence, the previous implies that the surface molecular structure should also play an important role in the catalysis of ODH [38].

1.5.2.3 Textural properties of the support

The phosphorous modified catalysts were found active in the ODH of EB to ST [2,19,22-23,35,38]. The catalyst preparation method in the Chapter 5 of this research is based on a solid state reaction between the support structure and the impregnated phosphorous solution. The reaction between the phosphate and the support, which is already extensively investigated [19,39-41], can yield several structures. An overview of the different surface groups resulting from the reaction during calcination are given in Figure 13.

For all the different phosphorous containing surface active groups, the oxygen atom of the phosphate molecule has bonded with a silica atom on the surface of the silica support. From Figure 13, it becomes clear that the phosphate ion can either bond with one, two, or three silica atoms. Furthermore, oxygen bridges can be formed between two phosphate ions. For supports containing alumina, the aluminium atom can coordinate the phosphate group.

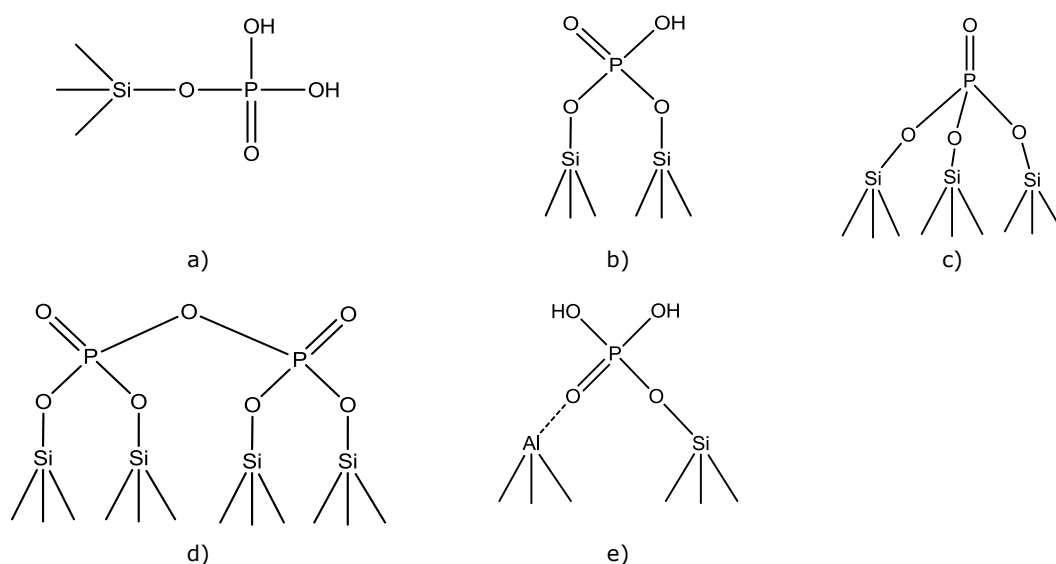


Figure 13. Possible surface active groups resulting from the impregnation with H_3PO_4^- : a) [19,42], b) [42,43], c) [43], d) [19], e) [44].

1.6 Process related pitfalls in scientific research

Constraints given by the process are not frequently accounted for in scientific research. However, they are decisive in whether or not a new process route can be economically feasible. In this section some important process related aspects regarding the ODH reaction experiments are discussed for the ODH of ethylbenzene in relation with industrial application.

1.6.1 Selectivity

In contrast to direct dehydrogenation process, currently commercially used to produce styrene, the ODH process consumes oxygen. This means that in the case

the selectivity to styrene is not 100%, CO_x can be formed in combination with mainly toluene and benzene, which are also being formed in direct dehydrogenation. Benzene and toluene can be separated from the styrene product and sold as by-products, although it increases the operational and investment costs. However, when CO_x is produced, EB feedstock is simply combusted.

Moreover, when ethylbenzene is converted to CO_x , eight times more oxygen is consumed compared to ODH to styrene due to the stoichiometry of the reaction. This has an influence on both the oxygen availability for the oxidative dehydrogenation reaction, influencing the maximal conversion, as well as the temperature control of the process. This has effect on the temperature control because the burning of ethylbenzene to CO_x is highly exothermic, especially compared to the ODH. The high exothermicity is due to stoichiometry, which is a problem particularly in a fixed bed reactor which is known for their poor heat transfer [45].

Limited selectivity to styrene is one of the main issues in the oxidative dehydrogenation of ethylbenzene. Activated carbons [33-38,48,52-59], carbon nanofibers [60-67], onion-like carbons [68-70], diamonds [56,58,70], nanofilaments [60], graphites [37,58,60,64], multiwall carbon nanotubes (MWCNTs) [56,58,66,69-79], and other type of carbon materials or mixtures of the above mentioned [80-84] were studied for this reaction widely. It is generally found that these materials are readily active and selective; the reported selectivities are moderate lying between 55-85 %. Only in some cases the reported selectivity is exceptionally high, in the range of 90-97% [58,76,77].

There are other two types of catalysts based on phosphorous such as metal pyrophosphates [23,26,85] and phosphates [2,26,39,49,85-91], or P-supported silica [19,26] that have been reported to be active and selective for EB ODH. However, the catalyst's stability under industrially relevant conditions is unknown and more insight in this direction is needed to prove its commercial viability.

The styrene selectivity obtained using Lewis acid-based γ -alumina is relatively low for commercialization, up to 70%, compared to the commercial process of steam dehydrogenation (ST selectivity >95%). Few examples indicate that the acidity enhancement of γ - Al_2O_3 by H_3PO_4 [26] or HBO_3 [92,93] has a positive impact on the styrene yield.

To commercialize the EB ODH process, it is needed to develop a catalyst which will have higher selectivity and stability than traditional catalyst for direct dehydrogenation. Since the K-promoted Fe_2O_3 catalyst for the conventional dehydrogenation process is highly selective to styrene, typically >97%, and stable [16], developing a selective and stable catalyst for oxidative dehydrogenation process is a rather ambitious target.

1.6.2 O_2 :EB ratio

The O_2 :EB ratio has an influence on the safe operation of a ST production plant in the case of ODH. It is preferred that the reaction mixture always stays outside of the flammability limits of ethylbenzene. At 30°C the lower flammability limit (LFL) of ethylbenzene in air is 1%, and the upper flammability limit (UFL) is 6.7%. The choice of 10 vol.% oxygen with 10 vol.% ethylbenzene gives a safe operation in all parts of the plant [11]. In addition, 100% oxygen conversion is desired, to prevent flammable mixtures in purge streams and on the distillation trays.

1.6.3 Stability

After selectivity, probably one of the most important aspects of industrial catalyst development is stability and hence the catalyst lifetime. Since a new catalyst bed is

often a very large capital expenditure, the stability of a catalyst can determine whether a catalytic process is economically feasible or not [46].

Under the reported reaction conditions, and time on stream, most of the carbon-based materials are stable with the exception of the activated carbons that are steadily decomposed [36,38,56,73]; the rate of gasification/burning is faster than that of the coke build-up. Some of the most stable systems are the carbon nanotubes and ordered mesoporous carbons, though they show a pronounced initial deactivation in 5 h [56]. Su et al. reported a decay from 90 to 70% EB conversion in a time frame of 5 h as well [79]. A similar initial deactivation was observed for furfuryl alcohol-based CMK-3 type carbons [56,79].

The deactivation of the catalysts based on the inorganic supports due to excessive coking is still a major concern [94] as well as enhancing the selectivity; the conventional process achieves extremely high selectivity to ST. Two types of instabilities have been found for the metal pyrophosphates, phosphates, or P-supported silica catalysts in the EB ODH. In time on stream having a maximum in the conversion curve after that it drops [23]. Other type of instability observed after each in-situ regeneration ($\sim 2-4\%$ selectivity and conversion) [95]. The main source of deactivation can come from the support itself under the reaction conditions that have a steam concentration up to 10 vol. %.

In general, catalytic tests of only 5-10 hours are reported in many publications and conclusions are drawn about the performance of the catalyst [19,22,25,34,37,38,40,47]. However, this performance can seriously deteriorate with longer time on stream (TOS). Therefore, this research focuses on longer TOS to see whether a catalyst is interesting from the industrial point of view.

1.6.4 Space velocity

In order to have a laboratory scale experiment which is comparable with an industrial scale, it is important to choose a comparable space velocity. Since industrial space velocities are in the range of 2000-20000 h⁻¹ (GHSV) [46], having a much lower space velocity deteriorate the industrial relevance of the experiment.

1.7 Concluding remarks on the ODH process

Despite over forty years of research, ODH for styrene production has never come further than the experimental state for several reasons. Looking at Table 2 the following aspects stand out as infeasible for industrial scale-up of the discussed catalysts:

- Many publications report a selectivity that is unsatisfactory, especially since CO_x is formed, which drastically deteriorate the process economics.
- Most experiments only show the first few hours of the reaction, ignoring the deactivation of the catalyst on a longer timescale.
- O₂:EB ratios are often not stated or too high for industrial purposes. If not all oxygen is converted during the reaction, a high temperature mixture of hydrocarbons and oxygen is flowing downstream of the reactor. It causes explosion risks in the reaction and distillation section of the process.
- Gas hourly space velocities are often not reported or too low compared to industrial processes.

Thus, from the comparison it is evident that a reliable evaluation is needed in terms of activity, selectivity, and stability under industrially relevant conditions. Note that no one has even been able to reproduce the impressive results with PNQ and PPAN with the selectivity nearing 100% (Table 2).

Table 2. ODH reaction results of various catalyst systems from literature

Catalyst	<i>T</i> [°C]	<i>S_{ST}</i> [%]	<i>X_{EB}</i> [%]	GHSV [h ⁻¹]	TOS [h]	O ₂ :EB	Ref.	Year
PNQ	200	100	2.1	21.6	N/A*	N/A *	[21]	1973
PPAN	325	≤100	≤80	N/A *	7	N/A *	[47]	1979
SnO ₂ -P ₅ O ₅	450	83	32	N/A *	N/A *	0.75	[39]	1981
H ₃ BO ₄ /alumina	500	88.3	77	3333	7	0.88	[22]	1981
Zr-phosphate	450	86	55	N/A *	16	1	[23]	1983
Pr/Mo promoted Al ₃ O ₃	500	86	67	900	10	0.5	[40]	1987
Zr(HPO ₄) ₂	350 450	90	50	N/A*	8	0.44-3.21	[25]	1988
NaOAc/Al ₂ O ₃	450	32	65	2655	45	1	[24]	1988
Ce ₄ (P ₂ O ₇) ₃	550	89	71	675	25	1	[26]	1988
Mg ₂ P ₂ O ₇	530	93	71	360	25	1	[26]	1988
Ce phosphate	605	90	76	1120	25	1	[26]	1988
Carbon molsieve	350	90	80	N/A *	20	5	[48]	1990
Zr/Sn phosphate	500	83	64	N/A *	20	1	[49]	1991
Activated carbon	350	70	20	N/A *	5	1667	[37]	1993
Activated carbon	350	73	48	5310	5	1667	[34]	1999
MWCNT	450	68	28	N/A *	4	1	[38]	2004
Activated carbon	450	83	41	N/A *	4	1	[38]	2004
CaO/SiO ₂	450 550	83	60	112	6	1.2	[19]	2005
P/CaO/SiO ₂	450 550	91	72	112	6	1.2	[19]	2005
Hierarchical carbon	300	90	22	N/A *	25	3-7	[50]	2012
γ-Al ₂ O ₃	475	86	41	3000	68	0.2/0.6	[51]	2014

*N/A: not available.

1.8 Thesis aim and overview

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 (ODH) of ethylbenzene (EB) to styrene under industrially relevant conditions. The main objectives are to improve styrene selectivity and catalyst stability, and to establish structure-performance relations. Regarding selectivity, the catalyst should show at least comparable selectivity to the direct dehydrogenation catalysts (i.e. >95%). This is especially relevant when CO_x 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, 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-promoted catalysts.

In the **Chapter 1** (Introduction) an overview of styrene production processes is presented, and the oxidative dehydrogenation process is discussed in detail. Various process-related aspects (i.e. selectivity, O₂:EB ratio, stability, 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 on the oxidative dehydrogenation of ethylbenzene to styrene is

discussed. A systematic study was performed in a 6-flow reactor set-up. Catalysts were characterized in detail.

In **Chapter 3**, a systematic study on the use of carbon-based materials, home-made carbon-silica hybrids, commercial activated carbon, and nanostructured multi-walled carbon nanotubes (MWCNT) for the oxidative dehydrogenation of ethylbenzene is reported. Special attention was given to the reaction conditions. Relatively concentrated EB feeds (10 vol. % EB), a limited excess of O₂ (O₂:EB=0.6), and lower temperatures (425-475 °C) in comparison with the commercial steam dehydrogenation process were applied.

In **Chapter 4** a strategy to enhance the thermal stability of home-made carbon-silica hybrids is proposed. It involves P-addition before the pyrolysis. In this study, the effects of P addition on a furfuryl alcohol based silica hybrid were investigated. The performance of the P-modified hybrid catalytic materials was compared to state-of-the-art P/SiO₂ and MWCNT. In addition, the catalyst stability under the ODH reaction conditions was evaluated from the apparent activation energies of the combustion reaction.

In **Chapter 5**, the feasibility to regenerate MWCNT under mild conditions is discussed. The regeneration method is described in detail, and the effect of the regeneration time on the pore volume and surface area was investigated.

In **Chapter 6** the effect of phosphorous addition to the various inorganic supports for ODH is described. The performance of various bare supports (silicas, aluminosilicate, zeolites, and zeolites with low alumina content) and the corresponding phosphorous-based catalysts is presented. The fresh, spent and regenerated catalysts were analysed with various techniques and the results are discussed.

1.9 References

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