

Chapter-1

Introduction (Styrene synthesis)

1.1 History

Styrene (St) is one of the most important monomers in modern petrochemical industry. The world production at present is approximately 20 million tons per year. The styrene process was developed in the 1930s independently and simultaneously by BASF in Germany and by DOW Chemical in the USA. St is mainly used for the production of many different polymeric materials, the most important being polystyrene, styrene-acrylonitrile and acrylonitrile-butadiene-styrene (ABS). Another important application is in producing styrene-butadiene latex [1-3].

St is produced in industry mainly by two processes:

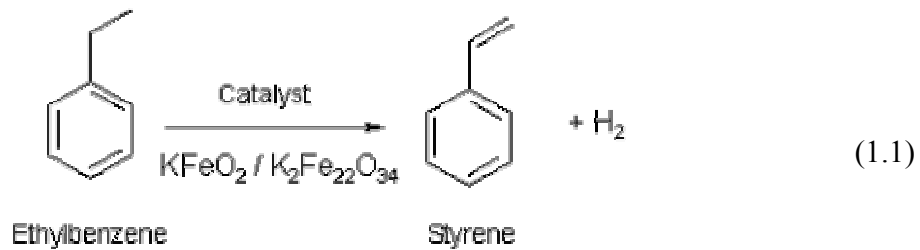
- I. dehydrogenation of ethylbenzene (EB) in presence of steam over iron oxide based catalysts
- II. as a by-product in the epoxidation of propene with ethylbenzene hydroperoxide and Mo complex-based catalysts.

The former process (I), accounts for more than 90% of the worldwide capacity. The catalytic dehydrogenation route, in which the potassium promoted iron oxide catalyst is typically used since 1957, produces most of the St. The process can be run industrially either adiabatically or isothermally over a fixed bed reactor in which the reactants are passed over the catalyst bed employing radial or axial flow [1,3].

Several catalysts, such as cobalt, copper, iron and zinc oxides, have been studied, both with and without promoters, but the potassium promoted iron oxide catalyst was found particularly efficient with respect to both selectivity and activity [2,3].

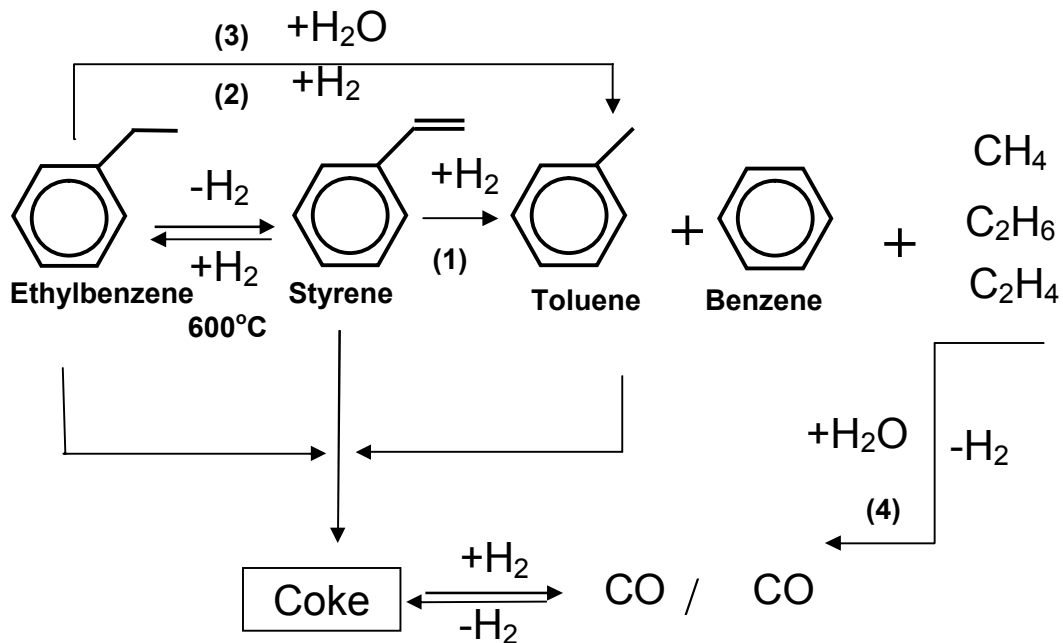
1.2 Reaction thermodynamics

The dehydrogenation reaction of EB to St (equation 1.1) is endothermic ($\Delta H=129.4$ kJ/mol) and equilibrium limited [4]



At room temperature, the reaction equilibrium is located far towards the educts side. It can be shifted towards the product side by increasing the temperature, which increases the equilibrium constant K due to the van't Hoff relationship and by reducing the pressure, since two moles of product are formed from one mole of EB. Therefore the technical St synthesis is run at around 600°C with an excess of steam, the steam-EB mixtures has a molar ratios from 5:1 to 12:1. Styrene plants run their reactors under isothermal or adiabatic conditions with flow rates that ensure short contact times in order to prevent polymerization of St [2]. The equilibrium EB conversion at 600°C and 0.1 bar pressure is $\sim 83\%$ [6], and conversions between 50 and 60% are obtained in technical reactors. The typical byproducts of the EB dehydrogenation are ($\sim 1\%$) benzene and ($\sim 2\%$) toluene formed by catalytic dealkylation (1) and hydrodealkylation (2) of EB, respectively, or they also can be formed by steam dealkylation (3) as shown in scheme (1).

All these reactions are accompanied by the formation of coke that can deactivate the catalysts. This coke is removed by combustion with steam according to the water-gas shift reaction (4) (scheme (1)) [7].



Scheme (1). Reaction network (products and byproduct) in the dehydrogenation of ethylbenzene. Toluene and benzene are formed by (1) dealkylation reaction, (2) hydrodealkylation reaction and (3) steam dealkylation. The Coke formation and gasification with steam is also shown (4).

The dilution of EB with superheated steam is believed to have several desired advantages for the styrene synthesis [1-3]:

- Shift of equilibrium towards higher EB conversion, (reduce educts partial pressure).
- Supplies part of the heat needed for the endothermic reaction.
- Decrease carbonaceous deposits by steam reforming reaction.
- Avoid catalyst over reduction and deactivation by controlling the valence state of iron i.e. prevent reduction to metallic state and limiting it to Fe_3O_4 under reaction conditions.

1.3 Reaction kinetics and mechanism

The kinetic aspects of the EB dehydrogenation were first investigated by Carra and Forni [8]. They described the reaction by a unimolecular Langmuir-Hinshelwood mechanism, where the reaction rate depends on the adsorption-desorption equilibrium of EB and St. The preferred adsorption of St can lead to a site-blocking effect by the product. These findings were supported by further studies of Lebedev et al. [9], Hirano [10,11], and Goodman [12].

It is believed that water vapor does not participate in the reaction itself, i.e. not involved in the rate determining step (RDS) of the reaction mechanism, but acts purely as inert dilution agent. However, as discussed above, it prevents the formation of inactive carbonaceous surface deposits and the reduction of the iron oxide to metallic iron by the produced hydrogen from reaction. Whereas Carra and Forni [8] assume one type of active sites generating all products in parallel reactions, several specialized reaction sites were postulated by Hirano [11]. For potassium promoted catalysts activation energies ranging between 120 and 190 kJ/mol were found. Since the activation energies for unpromoted α - Fe_2O_3 catalysts were similar (150 to 170 kJ/mol) [8, 11, 13, 14] identical active sites for the St formation on potassium promoted and unpromoted iron oxide catalysts were proposed [12, 14].

Muhler [15] has proposed that the active catalyst exposes a surface containing Fe^{3+} ions and K^+ ions at a ratio of 1:1, which was already suggested in the model of Lee [2]. In analogy to the oxidative dehydrogenation of butadiene over MgFe_2O_4 catalysts [16], a two step mechanism associated with an acidic and a basic site is postulated for the

dehydrogenation of EB over iron oxide and other transition metal oxide catalysts [15] [17]. Such a reaction scheme was also previously proposed by Muhler [18].

The C-H groups of the EB-ethyl group get deprotonated at basic oxygen sites and two hydroxyl groups are formed at the surface [19]. Simultaneously or subsequently an electron transfer to acidic Fe^{3+} sites is required before the styrene product molecule can desorb from the catalyst surface. Finally, the hydrogen atoms forming the two hydroxyl groups somehow leave the catalyst surface, the reduced Fe^{2+} species get reoxidized to Fe^{3+} , and the basic oxygen sites are reestablished for the next turnover cycle.

This picture agrees with results from an infrared spectroscopy study, where St formed by EB dehydrogenation was observed to be bonded to the catalyst surface through the vinyl group, whereas St adsorbed from the gas phase was bound via the aromatic ring [14]. In the proposed active KFeO_2 surface phase, potassium saturated Fe-O bonds increase the basicity of the oxygen sites. They also must be located in an adequate geometry with respect to the acidic Fe^{3+} sites, so that an effective deprotonation of the EB becomes possible.

1.4 Industrial catalyst composition

The dehydrogenation of EB to St in industry is carried out over potassium promoted iron oxide catalysts [4]. About 23 million tons of St are produced per year worldwide [5], which makes even small improvements of the catalysts profitable. An extensive review on the development of St synthesis catalysts was first published by Lee in 1973 [2], a recent review can be found in reference [2]. Potassium was found to increase the activity

of pure Fe_2O_3 (hematite) catalysts by one order of magnitude, and is believed to play a role in the removal of carbonaceous surface deposits, by catalyzing the combustion of coke with steam [2,11,12]. Potassium carbonate (K_2CO_3) is believed to be the active site for the coke gasification process [20,21].

Technical catalysts are prepared from about 80 wt% of iron oxide Fe_2O_3 (hematite) and at least 10 wt% of potassium oxide. Small amounts of alumina and chromia act as structural promoters and increase the lifetime of the catalysts [6]. Oxides of V, Ce, W or Mo improve the selectivity, but their effect is only moderate [11]. Therefore any catalyst model can be restricted to systems consisting of iron and potassium oxides.

An interesting question is why potassium is clearly the most used alkali promoter in commercial styrene catalysts. Mross [20] indicates that this is most probably a result of secondary effects. Under operating conditions (part of) the iron oxide exists as Fe_3O_4 (magnetite). Smaller alkali ions like, e.g. Li^+ can more easily migrate into the magnetite lattice and are no longer available for the gasification reaction. Larger ions, such as Cs^+ , catalyze the gasification reaction so strongly that also more St is gasified, resulting in a lower selectivity. Another important effect, that has to be taken into account, is the melting point of the alkali compounds present on the catalyst. Mross [20] points out that the activity for graphite gasification is approximately inversely proportional to the melting points of the carbonates, i.e. $\text{Li}_2\text{CO}_3 > \text{Cs}_2\text{CO}_3 > \text{Rb}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3$. Even the anion with which the alkali metal was formally associated was considered to be a factor of importance for the gasification activity.

After starting the catalytic reaction in a steam-EB mixture the EB conversion to St increases gradually. The steady state is reached within 20 hours time on stream [11,22]. This indicates formation of the active phase under reaction conditions. Mross proposed the working catalyst to consist of Fe_2O_3 , $\text{K}_2\text{Fe}_{22}\text{O}_{34}$, and Fe_3O_4 covered by a liquid film of KOH [20], a model that was ruled out later on. Hirano first proposed an active KFeO_2 phase to exist, based on X-ray diffraction (XRD) measurements on spent and "steamed" catalysts in the absence of air [11]. This proposal was also supported later by Muhler et al., who performed a detailed study on the catalyst precursor and on the working catalyst, applying a variety of in-situ and ex-situ techniques [15,18,22]. The precursor material consists of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) and the ternary $\text{K}_2\text{Fe}_{22}\text{O}_{34}$ phase which has a cubic crystal structure similar to the spinel structure of Fe_3O_4 (magnetite). Muhler proposed that under reaction conditions the active catalyst phase is formed, which he believes that it could be of a thin KFeO_2 layer supported on a solid solution of $\text{K}_2\text{Fe}_{22}\text{O}_{34}$ in Fe_3O_4 , and that $\text{K}_2\text{Fe}_{22}\text{O}_{34}$ phase could act as a storage medium from which the active surface is continuously supplied with potassium ions. Muhler found from ISS measurement that the ratio of K to Fe is 1:1 in the active phase and refer it to the KFeO_2 , which is not completely true as the recent characterization of different iron-potassium phases showed.

1.5 Catalyst deactivation

For economical reasons most styrene production units have large capacities (in excess of 400,000 t per year). The catalyst slowly deactivates and typically needs to be replaced every 1-2 years. In view of the process scale this is a costly operation and, hence, much

research has been dedicated to understanding of the deactivation mechanism and to developing possible method for preventing this deactivation. From a survey of almost all the literature on the studies done on this reaction four main reasons are generally brought forward for the catalyst deactivation [1] which are:

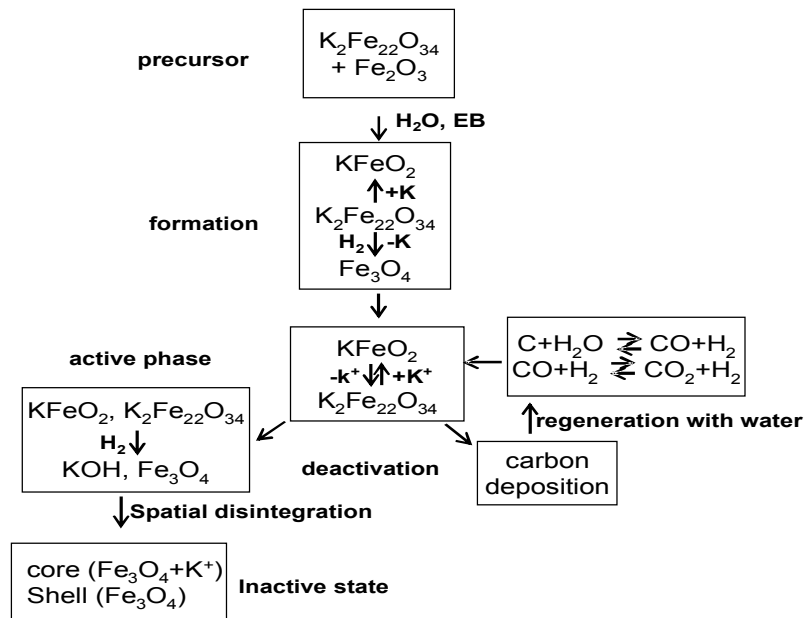
1.5.1 Coke deposition

The amount of coke deposited on a typical (promoted) iron oxide catalyst during EB dehydrogenation depends on several factors. Besides the specific catalyst and promoters, important features are the steam to oil ratio (steam/aromatic ratio, usually designed as S/O) and the temperature used. When lower S/O ratios and higher temperatures are used [23-25], this leads to higher coke levels. Regeneration is done by continuous gasification by steam. Often K_2CO_3 is proposed to be the catalyst for the coke gasification. Careful review of the literature data indicates that a steady state layer of coke is always present during typical styrene synthesis conditions.

1.5.2 Loss or redistribution of promoters

As already indicated, alkali metals are important promoters for the gasification of carbonaceous deposits. The most applied promoter in St synthesis is potassium, which as mentioned earlier plays many roles in this process. It is not surprising that its loss, changes in composition or migration will alter the catalytic properties of the iron oxide. At reaction conditions the potassium compounds, especially KOH, are slightly volatile, leading to a gas-phase transport to the outlet of the reactor. Also, potassium migrates from the exterior to the core of the catalyst pellet due to a temperature gradient resulting from the endothermicity of the reaction Lee [2,7]. Also recent studies by Holmeid et.al, indicated that potassium could be lost also as neutral atoms or as excited states [26,27]

Muhler investigated the life cycle of the catalyst and proposed a model which is shown schematically in scheme (2). The potassium migration causes a continuous solid-state transformation of the catalyst during its lifetime. An irreversible deactivation is caused by spatial disintegration of the iron oxide and the potassium compound leading to a core of potassium rich Fe_3O_4 and a shell of only Fe_3O_4 , by the total loss of potassium, and by the reduction of KFeO_2 and $\text{K}_2\text{Fe}_{22}\text{O}_{34}$ into Fe_3O_4 and KOH . A reversible deactivation of the catalyst is caused by blocking of active surface sites with CO_2 adsorbed in competition with the reactant, as well as by the formation of inactive carbonaceous surface deposits. These species can be removed by a steam treatment. A catalytically active role of the carbonaceous species was never discussed in literature for the non-oxidative dehydrogenation process.



Scheme (2). Schematic of the life cycle of styrene catalyst with potassium and no other promoter additives as found from in-situ and ex-situ characterization work on the working catalyst by Muhler et. al [15].

1.5.3 Oxidation state

Hydrogen is formed (locally) at the catalyst surface, whereas steam and hydrocarbons are present in the feed. This results in a complex and dynamic system, especially at the high temperatures (600°C) involved. Moreover, solid-state changes, that are kinetically slow, can still take place considering the typical lifetime of a St catalyst [2,28-32].

Overall, the feed composition is considered reducing at temperatures above 600°C. Lee [2] observed that the iron compound in a fresh catalyst consisted of mainly Fe₂O₃ (hematite) which is reduced to Fe₃O₄ (magnetite). He noted that Fe₃O₄ is more selective. This was also seen by Yang et al.. Muhler et al. found also that the KFeO₂ is also slowly reduced with time on stream to Fe₃O₄. However, he proposed that the K₂Fe₂₂O₃₄ could serve as a potassium storage medium supplying the surface with a near-monolayer coverage of potassium ions and preventing the reduction of Fe⁺³ ions. Irreversible deactivation occurs when the K₂Fe₂₂O₃₄ becomes exhausted.

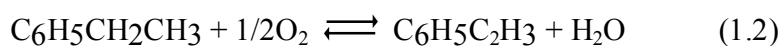
1.5.4 Physical degradation

The physical degradation of iron oxide catalyst during St synthesis has been recognized as an important problem [1]. The cause is closely related to the change in the oxidation state of the iron oxide (Fe⁺³ to Fe⁺²). Under reaction conditions the Fe₂O₃ is reduced to Fe₃O₄. Fe₂O₃ has a hexagonal lattice structure whereas Fe₃O₄ has a cubic lattice structure. This lattice structure change, along with the high mechanical forces in the catalyst bed, results in degradation or pulverization of the catalyst particles. Also, the slow density changes due to migration of the potassium promoter contribute to the weakening of the catalyst crush strength. Also the potassium depletion leads to higher coking levels and the pores of the catalyst can become plugged. The overall result of the above processes is that

the pressure drop over the catalyst bed becomes larger, which adversely affects the selectivity and the yield of the working catalyst [1,32]

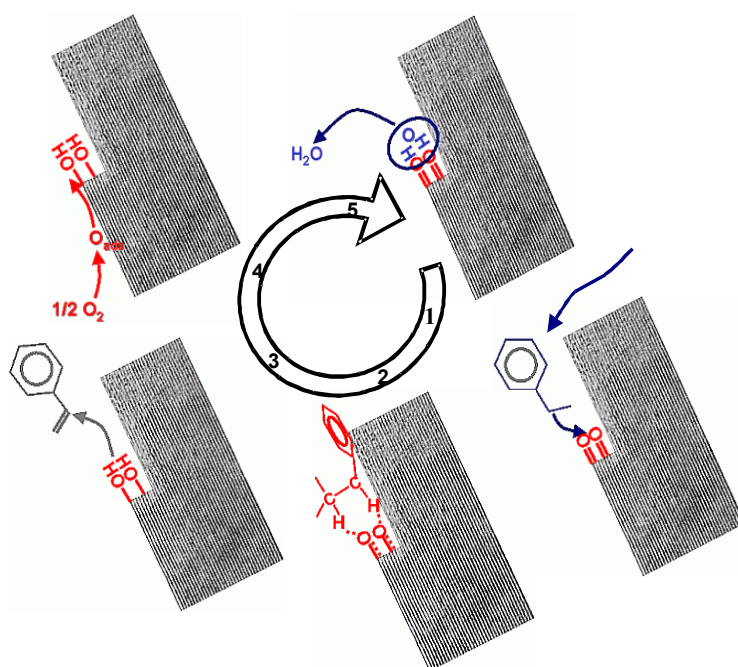
1.6 Alternative processes for styrene synthesis (Oxidative dehydrogenation of EB)

Oxidative dehydrogenation is one of the many alternative techniques which have been proposed to overcome some of the disadvantages of the styrene synthesis by EB dehydrogenation like the high endothermicity of the reaction and product separation. Alkhazov et al. proposed that carbonaceous deposits which were formed in the first hours of time on stream on the surface of acidic catalysts act as the real active centers for the oxidative dehydrogenation of EB to St [33]:



Since then, there has been a great deal of interest in oxidative dehydrogenation schemes [34- 37]. The formation of water as a byproduct makes the process exothermic and thermodynamically enables complete conversion. This also reduces the energy consumption for the St synthesis over iron oxide catalysts considerably. In more recent studies various carbon materials exhibited higher activities and selectivities than iron oxide based catalysts at much lower reaction temperatures than 600°C [38,39]. For example, 80% conversion and 90% selectivity were achieved at 350°C over ultrahigh surface area carbon molecular sieves [42]. The oxidative dehydrogenation of EB was investigated over various oxide compounds [43, 44] and phosphates [43-46], the carbonaceous layers that form on the surface were found to act as the true catalyst. This "active coke" is an organic polymer that is formed from EB and oxygen in the feed and contains carbon, hydrogen and oxygen. XPS and SIMS measurements indicated the

presence of quinone-like groups [47, 48]. The oxygen atoms in these quinone groups can dehydrogenate EB forming water as a product, as proposed in a speculative reaction mechanism by Emig [43] in scheme (3) [49,50]. About 50% of the surface is supposed to be covered by these carbonaceous species, after equilibrium between their formation and combustion has established. The formation of this active coke was found to depend on the surface acidity of the inorganic support [52, 53]. Basic substrates like magnesia and titania are nearly inactive, and very acidic sites are also ineffective [43, 54]. Generally, sites with a Lewis acidity of moderate strength are considered to form the active coke most effectively [46]. So far there is no evidence that carbonaceous overlayers act as the true catalyst for the non-oxidative dehydrogenation of EB over iron oxide based catalysts



Scheme (3). Schematic drawing of the catalytic oxidative dehydrogenation over carbon nanofilaments, 1- adsorption of EB, 2-dehydrogenation at basic centers, 3-desorption of St, 4- adsorption of oxygen and reaction with OH groups, 5- desorption of water