Comparison of single-bed oxidative dehydrogenation of ethylbenzene with double-bed using CO₂

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Abstract

The present study highlights the catalytic performance of 5 wt% Fe₂O₃ supported on sodium chromosilicate (5F/NCS) in a single-bed reactor for dehydrogenation of ethylbenzene with CO₂ and compares it with the catalytic performance of two subsequent catalysts (5F/NCS + industrial oxidation catalyst) in a double-bed reactor. The support of the target nanocomposite catalyst was obtained by hydrothermal treatment and subsequently was loaded with a medium amount of 5 wt% γ-Fe₂O₃. Structural and textural characterizations of the catalysts were performed by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, N₂ physical adsorption analysis, and Fourier-transform infrared spectroscopy. The catalytic tests revealed that 5F/NCS in the single-bed reactor had a high ethylbenzene conversion (> 54%) and a low styrene selectivity (> 70%). In comparison with this observation, in the double-bed reactor with the presence of oxidation catalysts, styrene selectivity increased significantly (> 91%), however; ethylbenzene conversion indicated a minor decrease (> 50%). The high styrene selectivity (> 91%) and styrene yield (> 46%) in the double-bed reactor were ascribed to the coupling reaction of ethylbenzene dehydrogenation and RWGS as well as the synergistic effect of Pt–Sn in the structure of oxidation catalyst.

Keywords Oxidative dehydrogenation · Styrene · Oxidation catalyst · Pt–Sn bimetallic catalysts · CO₂ as a soft oxidant · Lattice oxygen · Cracking reactions

1 Introduction

Styrene (ST) is one of the platform chemicals for plastic and petrochemical industries, utilized primarily for the synthesis of polystyrene and ST copolymers such as acrylonitrile–butadiene–styrene (ABS), styrene acrylonitrile (SAN), styrene–butadiene rubber (SBR), fibers, ABA resin etc. [1–6]. At present, there are two main processes for the manufacture of ST. In the first one, ST is produced as a side-product in the epoxidation of propene with ethylbenzene (EB) hydroperoxide with Mo complex based catalysts. The second one and also the most important manufacturing route to ST is by the direct dehydrogenation of EB on iron

oxide catalysts at 873–973 K, just below the decomposition temperature of the reactant [2, 6–9]. Because the reaction is highly endothermic and volume-increasing, a large amount of superheated steam is used to supply heat, decline the partial pressure of the reactants to shift the equilibrium to ST, and inhibit the buildup of coke or of coke precursors on catalyst surface to prolong the catalyst activity, and eventually keep the iron oxide in an appropriate oxidation state [8, 10–12]. However, the use of steam has a number of defects including waste of a large amount of latent heat of condensation during subsequent separation in the conventional process instead of being

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recovered, catalyst deactivation, and depletion of EB and ST by steam reforming [2, 8, 9, 13–15].

To overcome the mentioned flaws in the commercial process with steam many efforts have been put forward to improve the process by making it steam-free and applying lower temperatures. Therefore, other oxidants have been examined in oxidative dehydrogenation (ODH) of EB including dry air, O₂, CO₂, N₂O, and SO₂ [2, 5, 6, 16]. Dehydrogenation in the presence of O₂, however, requires less energy, it leads to burning a significant amount of valuable hydrocarbon [5, 17]. N₂O and SO₂ are hazardous gases and preferably they cannot be utilized in ODH of EB to prevent their pernicious effect on human and the environment [18]. On the contrary, CO₂ as a greenhouse gas, can decrease the partial pressure of reactants more effectively than steam, has the highest heat capacity among various typical gases, reduce energy consumption, accelerate the reaction rate, suppress the catalyst deactivation, and alleviate thermodynamic equilibrium limitations [1, 5, 6, 9, 14, 19]. Furthermore, it is widely believed that carbon dioxide works very well in EB dehydrogenation as the soft oxidant and diluent to improve both the conversion and selectivity. The order of catalytic activity and selectivity for ST according to carrier gas was CO₂ > N₂ > H₂O [20]. Additionally, industrial use of CO₂ is increasingly important in many aspects especially the greenness of the process where CO₂ is consumed during the process [6]. As a consequence, ODH of ethylbenzene with CO₂ as a soft oxidant has attracted a considerable attention [5, 13, 17, 19, 21–24]. ODH of EB (3) in the presence of CO₂ proceeds via two reactions [1, 2]: first EB is dehydrogenated to ST and H₂ (Eq. 1), subsequently CO₂ employed in this reaction reacts with H₂ produced in the EB dehydrogenation reaction to yield CO and H₂O via RWGS (Eq. 2). Moreover, CO₂ can act as coke gasifier according to (Eq. 4).

In past years, extensive efforts have been made in order to develop new catalysts for ODH of EB, since the commercial catalysts do not work effectively in such a coupling

system. The efficient catalysts for ODH of EB are mainly supported metal oxides, including Fe-, Cr-, V-, Ce-based oxides [12, 25]. Among them, vanadia and chromia exhibited high catalytic activity for the dehydrogenation of EB with CO₂ [26, 27]. In fact, the advantages of chromium in this particular process outweigh its disadvantages [28]. Additionally, effective supports for this reaction are based on inorganic metal oxides, MgO, SiO₂, CeO₂-ZrO₂, TiO₂-ZrO₂, MnO₂-ZrO₂, V₂O₅-CeO₂, SnO₂-ZrO₂, FeO_x-Al₂O₃, TiO_x-Al₂O₃ and CeO₂-ZrO₂ as an acid–base bi-functional support as well as catalyst [1, 9, 10, 12, 29]. Moreover, various zeolites as well as a wide range of carbonaceous materials, have been applied as the supports [11]. Based on the previous experiments [10], alkaline metals (Li, Na and K), alkali earth metals (Ca and Mg) and other elements (Sb and Cr) were introduced as the promising promoters

Previously, we have reported ZSM-5 type chromosilicates [30], and chromosilicate-based composites [31] as effective catalysts for ODH of EB in the presence of CO₂ and examined their performance (based on conversion and selectivity), stability (long-term use of catalysts up to three cycles without regeneration), and reusability. Also, previous study based on FTIR spectrum and TGA of the spent synthesized catalysts as well as SEM of the used industrial catalysts exhibited that the main culprit for the deactivation of dehydrogenation catalysts is partial reduction of Fe³⁺ ions (particularly reduction of the Fe-based catalysts to the magnetite-type [32]) in their structures [31]. It should be highlighted that based upon the mass loss of the spent catalyst after combustion from 300 °C up to 550 °C, during the TGA experiment, the amount of coke deposition for the spent catalyst was calculated to be 2.75 wt% of the total weight of the catalyst [31]. As maintained by the mentioned facts, authors decided to select one of the catalysts (5F/NCS (5 wt% Fe₂O₃ supported on sodium chromosilicate)) that had the lowest activity (the lowest ST selectivity amidst the composite catalysts—in a single-bed ODH reactor—70.86% [31]) in this process and attempted to improve its performance. As a consequence, the foremost objective of the present contribution is to compare catalytic activity of 5F/NCS in a single-bed ODH reactor with a double-bed reactor having two catalysts including 5F/NCS and industrial oxidation catalysts and discuss the primary reasons to enhance the catalytic activity. As the authors had previously conducted tests by a single-bed reactor, the double-bed reactor with an oxidation catalyst was a great choice; as oxidation catalysts would reinforce catalytic performance by eliminating hydrogen from the reaction environment—leading to higher ST selectivity.

2 Experimental section

2.1 Catalyst preparation

2.1.1 Preparing Na[Cr]ZSM-5 (NCS) as the support

As described in details previously [33], sodium chromosilicate was prepared by the hydrothermal procedure. In brief, first silicic acid and sodium carbonate were dissolved in distilled water and added slowly to the solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and sulfuric acid in water until pH of the solution was adjusted at 0.5. Further, pH of the mixture was modified at 9 using concentrated sulfuric acid. Afterward, TPABr was added; and the obtained gel was stirred continuously at room temperature for about 4 h. The crystallization of the prepared gel was made by hydrothermal treatment at 155 °C for 100 h. After crystallization, the synthesized samples were washed several times with distilled water and dried overnight in an oven at 120 °C. Finally, calcination was carried out for 5 h at 550 °C. In this contribution, sodium chromosilicate was washed with a large amount of distilled water to remove amorphous grains from pores. Thus, NCS_{BW} and NC_{AW} are referred to as sodium chromosilicate before washing and after washing with distilled water, respectively.

2.1.2 Preparing $\gamma\text{-Fe}_2\text{O}_3$

Synthesis of $\gamma\text{-Fe}_2\text{O}_3$ was started by adding in a drop wise manner of a NaOH solution (2.5 M) to an aqueous solution of iron (II) sulfate until the pH of the mixture was adjusted to 11. The reactants were maintained under constant stirring for 6 h, and the obtained solution (which was located in a heated water bath) split into a two-phase solution. The solid phase was afterward, centrifuged and washed with distilled water several times, dried at room temperature and calcination at 200 °C under air flow for 45 min.

2.1.3 Synthesis of $\text{Fe}_2\text{O}_3/\text{Na[Cr]ZSM-5(5F/NCS)}$

In order to maintain the phase and nature of Fe_2O_3 as well as to have an insightful comparison between pure iron oxide and composite, 5F/NCS was prepared via solid state dispersion (SSD) method [34]. 5 wt% of iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were mixed with a required amount of NCS in the presence of ethanol under vigorous stirring at room temperature until ethanol was evaporated during mixing. More importantly, to improve the interactions between precursors in mixed oxide catalysts, it is pivotal that precursors have an intimate contact with the least phase

Table 1 Chemical and physical properties of oxidation catalyst [TPC-R&D]

Chemical properties of oxidation catalyst		Physical properties of oxidation catalyst	
Pt	Max 0.20 wt%	Particle size	3 mm extrusions
Sn	Max 0.33 wt%	Side crush strength	> 2 MPa
Li	Max 0.14 wt%	Surface area	10 m ² /g
Fe	0.08 wt%	Pore volume	0.29 ml/g
Ca	0.01 wt%		
Cl	< 0.10 wt%		

segregation. All of which can be achieved by solid state preparation method [35].

2.1.4 Oxidation catalyst

Industrial oxidation catalyst (OC) was obtained from Tabriz Petrochemical Company-Research & Develop (TPC-R&D). There are a number of pretreatment processes for oxidation catalysts [36, 37]; however, the authors utilized OC without further purification. The chemical and physical properties of oxidation catalyst are given in Table 1.

2.2 Apparatus and procedure

Catalytic reaction of dehydrogenation of EB using CO_2 was carried out in a fixed bed quartz reactor. The single-bed reactor for ODH of EB contained only 2 g of 5F/NCS loaded between quartz beds and double-bed reactor for dehydrogenation and oxidation consisted of 2 g of 5F/NCS followed by 2 g of oxidation catalyst supported by quartz beds (see Scheme 1). The reaction conditions were the same for both catalytic reactions. The reaction was performed at 873 K and atmospheric pressure for 4 h. Before the start of the reaction, the catalyst was treated with the N_2 flow (100 mL.min⁻¹) from room temperature to 873 K at a heating rate of 145 K/h and kept at this temperature for 30 min then N_2 was replaced with CO_2 gas (36.64 mL.min⁻¹). EB was fed into the reactor at a constant rate (32.64 mmol.h⁻¹) by means of a syringe pump. The outlet vapor was condensed in a cold trap of an ice bath and analyzed by a Varian 3800 CX gas chromatograph apparatus using aflame inductivity detector (FID). EB conversion and ST selectivity are calculated as per the following (Eq. 5) and (Eq. 6), respectively:

$$\text{EB conversion} = \frac{EB_{in} - EB_{out}}{EB_{in}} \quad (5)$$

$$\text{ST selectivity} = \frac{ST_{out}}{EB_{in} - EB_{out}} \quad (6)$$

Scheme 1 Simplified schematic diagram of the double-bed reactor for dehydrogenation and oxidation of EB [30, 31]

where, EB_{in} is the amount of EB at the inlet and EB_{out} and ST_{out} are the amounts of EB and ST present in the product mixture respectively.

2.3 Characterization of catalysts

X-ray powder diffraction (XRD) patterns were recorded in an STOE X-ray diffractometer (Version PKS-2.01). The Cu K α radiation ($\lambda = 1.540598 \text{ \AA}$) was used and diffractograms

were collected with a 2θ step of 0.06 and a counting time of 1 s per step. Diffraction peaks recorded between 4° and 70° have been used to identify the structure obtained at 40 kV and 30 mA. Scanning electron microscopy (SEM) pictures were determined on a Philips XL-30 system equipped with an EDX detector on the samples coated previously with a thin layer of gold. Nitrogen adsorption and desorption isotherms were measured at 77 K on a BELSORP mini, BEL Japan Inc. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) model. The pore size distributions were obtained from the desorption branch of the nitrogen isotherms by the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) images were recorded on a 208 S PHILIPS microscope operated at 100 kV. Fourier transform infrared spectroscopy (FTIR) measurements were performed using a spectrophotometer (Tensor 27) over the wavenumber $4000\text{--}400 \text{ cm}^{-1}$.

3 Result and discussion

3.1 Morphology studies

SEM images of the NCS sample after and also before washing with water are shown in Fig. 1c,d respectively. It can be distinguished that NCS appears as well-structured coffin-type crystals possessing relatively large sizes (about $20\text{--}21 \mu\text{m}$). According to these SEM images of NCS samples, it seems that the growth of crystal grains occurred well. In spite of the formation of well-structured crystals, some amorphous grains can be detected, which could be as a result of incomplete crystallization of some particles or may be attributed to CrO_3 particles. In this work, the NCS sample was used as a support after washing it with

Fig. 1 SEM images of **a, b** Fe_2O_3 , **c** NCS after washing, **d** NCS before washing, and **e, f** 5F/NCS samples. TEM images of **g, h** 5F/NCS composite

Fig. 2 XRD patterns of the prepared samples; (a) γ - Fe_2O_3 , (b) NCS_{BW} , (c) NCS_{AW} , (d) 5F/NCS

a large amount of water for the purpose of removing the extra amorphous grains as much as possible. As mentioned in our previous work [31] after washing this sample with a large amount of water, it is possible to recognize the nature of the mentioned amorphous particles by performing SEM analysis. As it can be observed in Fig. 1c, a great deal of these particles can be removed which could be attributed to CrO_3 particles and the remaining particles which have no specific shapes can be related to amorphous grains of NCS sample. On the other hand, after loading of the Fe_2O_3 nanoparticles into the structure of the NCS sample (as the support) for preparation of the desired composite (5F/NCS) with 5% Fe_2O_3 (Fig. 1e, f), due to the interference of Fe_2O_3 nanoparticles, the mentioned extra grains on the NCS crystals increased. Regarding the fact that the SEM image of the Fe_2O_3 nanoparticles has as similar appearance (Fig. 1a, b) as the amorphous grains, this result can be expectable. Indeed, the TEM image of 5F/NCS sample (Fig. 1g, h) illustrates the highly concentrated agglomeration of the particles, with diameter around 10–20 nm.

It should be highlighted that conventional catalysts preparation methods such as impregnation, co-precipitation and sol–gel which are operated in aqueous environment, the intimate contact of precursors can hardly be controlled due to the inherent different solubility products and complex influencing factors (pH, concentration,

temperature, aging time, drying mode). On the other hand, solid state method enjoys advantages like simple operation, easy control of parameters and friendly to environment. Apart from the mentioned benefits of solid state process, large surface area and high porosity are very likely in case of catalysts prepared by this method [35].

3.2 XRD analysis

The XRD patterns of the obtained samples are illustrated in Fig. 2. For the purpose of comparison, Fig. 2 also contains the patterns of unsupported Fe_2O_3 and pure sodium chromosilicate (NCS) after and before washing with distilled water.

As can be seen in this image, XRD patterns of the prepared Na[Cr]ZSM-5 (NCS) confirms the formation of ZSM-5 zeolite structure with orthorhombic symmetry according to the literature [38], which can be detected by peaks at $2\theta = 7.94, 8.86, 23.10, 23.9$, and 24.45 illustrating (011), (200), (051), (033), and (313) planes of crystal structure, respectively. After loading the desired amount of γ - Fe_2O_3 , (5 wt%) for preparation of 5F/NCS composite, the main diffraction peak related to Fe_2O_3 can be detected at $2\theta = 33.7$ (see Fig. 2). Furthermore, the 5F/NCS characteristic peaks of sodium chromosilicate (NCS) as the support in the XRD pattern of the composite can be seen with a slightly lower

Fig. 3 **a** Nitrogen sorption isotherms of samples, **b** pore size distribution curves of samples

Table 2 Specific textural properties and catalytic activity of the prepared catalysts in EB dehydrogenation and oxidation at 873 K and CO₂ flow of 36.64 mL min⁻¹ [31]

Components	BET surface area (m ² g ⁻¹)	Average pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)	X (%)	Bz (%)	Tol (%)	S (%)	EB conversion (%)
5F/NCS	61.12	8.036	0.1228	38.63	10.43	5.60	70.68	54.66
5F/NCS+OC				46.09	2.32	1.16	91.87	50.17
NCS _{AW}	316.62			44.81	2.24	3.32	88.96	50.37
NCS _{BW}	307.74	2.2620	0.1740	46.38	1.24	1.87	93.72	49.49
Fe ₂ O ₃	36.10	17.31		46.85	12.29	3.67	74.59	62.81

X styrene yield, Bz benzene, Tol toluene, S styrene selectivity, EB ethylbenzene

intensity compared to that of the pure sodium chromosilicate confirming the formation of the composite.

3.3 Nitrogen adsorption isotherms and pore size distribution

For evaluation of the specific textural properties of the samples Brunauer–Emmett–Teller (BET) analysis was performed and thereby porous structure of the samples and their pore size distribution were investigated [39]. The adsorption–desorption isotherms and relating (BJH) pore size distribution curves of all samples are shown in Fig. 3a, b respectively, and the textural properties are presented in Table 2.¹ As can be distinguished in Fig. 3, and

in accordance with IUPAC Classification of Gas Adsorption Isotherms, all of the samples reveal a type IV isotherm possessing a distinct step confirming the presence of mesoporosity [40]. The steep increment of adsorption step at low relative pressure ($P/P_0 < 0.1$) (except for Fe₂O₃ nanoparticle), is due to the presence of micropores in these samples. At medium amounts of P/P_0 , a capillary condensation step and an H3-type hysteresis loop were detected, indicating the appearance of slit-like pores in the structure as a consequence of the loose gathering of plate-like particles [41].

N₂ adsorption and desorption experiments on NCS sample lead to a step-wise desorption isotherm, indicating bimodal porosity, in spite of the fact that the adsorption branch exhibits only one step in which the size of both the open and blocked mesopores are illustrated (Fig. 3). It is noteworthy that the step-wise desorption isotherm exists as the encapsulated mesopores can empty at a lower pressure compared to the similar open pores [42].

¹ All of the BET data which has been gathered in the Table 2 was reported by the operator of the analysis. For some of the samples, average pore diameter was not reported.

Fig. 4 FTIR spectra of (a) γ -Fe₂O₃, (b) NCS_{BW}, (c) NCS_{AW}, (d) 5F/NCS

The pore size distribution was provided by using the Barret-Joyner-Halenda method via BJH analysis of adsorption isotherm data and presented in Fig. 3b.

3.4 FTIR analysis

FTIR spectra of the obtained samples are presented in Fig. 4. For the purpose of comparison, Fig. 4 also contains the spectra of unsupported Fe₂O₃ and pure sodium chromosilicate (NCS) after and before washing with distilled water. The spectra of chromosilicate-containing samples have the great similarity with the spectrum of ZSM-5 including the presence of zeolite-like building units e.g. the characteristic band of the pentasil structure (double ring vibration) possessing five-membered ring at around 549 cm⁻¹ and bending vibration of T–O–T bend at about 445 cm⁻¹ which are clearly detectable in the spectra of NCS-based samples. Furthermore, asymmetric stretching vibration of the T–O bond at around 1237 cm⁻¹ for NCS sample can be related to external linkages between TO4 tetrahedrals. Moreover, the presence of the peaks at 449 and 638 cm⁻¹ for nanoparticles of Fe₂O₃ and also its composite with NCS (5F/NCS) are attributed to the stretching vibrations of Fe–O bond.

3.5 Catalytic performance of the prepared samples

Vapor phase dehydrogenation of EB with CO₂ was carried out at 873 K and 1 atm over 5F/NCS catalyst in a single-bed reactor, and its results were reported in our previous study [31]. Herein, we report the dehydrogenation followed by oxidation of EB in a double-bed reactor with the same conditions. For a better comparison between two catalytic tests, the results have been brought together in Table 2. As it is obviously seen, ST yield and selectivity in the double-bed reactor have been improved significantly from 38.63 to 46.09 and 70.68 to 91.87, respectively. However, EB conversion has a minor decrease in double-bed reactor compared to single-bed.

Synthesized 5F/NCS catalysts in both reactors loaded with 5 wt% of iron oxide exhibited a remarkable conversion of EB. In case of ODH to obtain ST by using iron-based catalysts, owing to Fe³⁺ ions as active but not necessarily selective components, high EB conversion was generally expected. Moreover, it has been discovered that oxygen deficiency of iron oxide in the supported catalyst is one of the most important factors in promoting the catalytic activity in the presence of CO₂. Oxygen deficient sites of the supported iron oxide catalyst (such as NCS supported γ -Fe₂O₃) seem to produce CO efficiently from the CO₂ dissociation, and the adsorbed oxygen on the catalyst surface can also play a role on hydrogen abstraction from EB [20, 43] leading to high conversions for both cases. During dehydrogenation of EB in the absence of an oxidant, the lattice oxygen of the catalyst takes part in H₂ abstraction to form water. After the complete consumption of lattice oxygen of the catalyst surface, the rate of water generation declines with a gradual increase in the generation of molecular H₂ [44]. On the other hand, by the introduction of CO₂ as a mild oxidant that constantly supplies lattice oxygen and therefore avoids H₂ formation [45, 46].

As mentioned previously, CO₂ is more attractive compared to other oxidants such as O₂, NO₂ and SO₂ because of being widespread, less harmful, low cost and mild oxidizing features [47, 48]. In addition, from studies performed on ODH processes with CO₂ we learned the oxygen vacancies in bulk catalysts could abstract the oxygen from CO₂ molecules, forming dissociated oxygen and CO. The formed oxygen vacancy could be re-oxidized by CO₂, and the catalyst returned to its original state [49]. As reported, heteroatom doping was an effective method for improving the lattice oxygen content and oxygen mobility of transition metal oxide catalysts. Hence, doping iron, vanadium and chromium on the Fe₂O₃/γ-Al₂O₃ leads to higher oxygen mobility and thereafter higher catalytic activity [47]. Watanabe et al. investigated the effect of the reduced state of the BaZrO₃ (BZO) catalyst by electron-spin resonance (ESR) spectra and the effect of prerduction by

Scheme 2 Reaction schemes for the production of side-products of EB dehydrogenation reaction (benzene and toluene)

H₂. Their efforts culminated by two following Eqs. (7) and (8) [32].

Where $\text{O}_{\text{lat}}^{2-}$ and V_{ox} denote a lattice oxygen and an oxygen vacancy in the catalyst, respectively. Based on the mentioned reactions, the formed oxygen vacancy could be re-oxidized by CO₂, and the catalyst returned to its original state. According to these explanations, presence of iron oxides in case 5F/NCS + OC leads to the increasing defect-site concentration, and the defect-site is the active site for the EB dehydrogenation over Fe₂O₃ [32]. This fact clearly explains the difference between catalytic performance of 5F/NCS + OC and NCS_{AW} which they have nearly same conversion but the former catalyst is more active (refer to Table 2).

As it was previously mentioned in the introduction section, according to reaction (Eq. 1), dehydrogenation of EB produces H₂ which can be removed by RWGS (Eq. 2) and hence increases ST selectivity. However, according to the results for single-bed catalytic test, 5F/NCS suffers from a low selectivity which can be attributed to the fast transformation of Fe³⁺-containing iron oxide phases (red state) to magnetite (black state) when catalyst surface is exposed to ethylbenzene at 873 K for the first time (Eq. 9). According to the reports published in literature [1, 13, 19, 25, 32], well dispersion of active phase on support and redox properties of catalysts play a pivotal role to achieve higher performances, but in this case, we rule out these factors; because both dehydrogenation catalysts have the same structure. As a consequence, the role of oxidation catalyst needs to be highlighted in this work for high selectivity toward ST.

3.6 Role of oxidation catalyst

A glance at Table 2 shows that in the single-bed via only ODH reaction with CO₂, the amount of main side-products, benzene and toluene produced by cracking (Eq. 10) and

hydrogenolysis (Eq. 11) [9, 50] are enormous compared to the double-bed reactor in the presence of ODH and oxidation catalysts.

It is accepted that more acidic catalysts generally support cracking of hydrocarbons expediting generation of more undesired byproducts and coke which subsequently leads to catalyst deactivation [9, 12]. The effective ODH with CO₂ proceeds on acid–base sites on the catalysts. Wang and coworkers [51] explored from their study that the formation of toluene and benzene are predominately because of the influence of strong acid–base sites on the surface of the catalysts. Strong basic sites can extract the β -H of the adsorbed EB which speeds up the division of side chain C–C bond contributing to the formation of toluene (Eq. 9), while the strong acid sites extract α -H of EB and accelerate the division of phenyl-C bond leading to the production of benzene (Eq. 8) (Scheme 2). In the commercial production of ST, following dehydrogenation of EB and production of H₂, oxidation catalyst plays a critical role by the subsequent reaction (Eq. 12) [TPC-R&D]:

In our study, this reaction proceeds by CO₂ via RWGS (Eq. 2). This reaction clearly demonstrates the further removal of hydrogen from the reaction environment, and consequently results in higher selectivity toward ST compared to the single-bed reactor.

Two major elements of oxidation catalysts are Sn and Pt which seems to have an influential role in the performance of the catalyst. Both elements have been extensively investigated in the dehydrogenation of light alkanes [52, 53] and now it is proven that alloyed Sn-Pt in the structure of the catalyst increases conversion and selectivity, prevents metal sintering, and suppresses coke formation. Pham et al. [52], pointed out that the addition of Sn as a promoter helps to modify both the Pt active phase and the support. Since the Pt–alkene interaction is stronger than

the Pt – alkane interaction, undesired side reactions such as hydrogenolysis and isomerization can occur; Sn weakens the Pt – alkene interaction without weakening the Pt – alkane interaction and, therefore, suppresses the side reaction. This is how Sn is thought to influence the selectivity of the catalyst. With this explanation, the same situation can be envisaged in EB dehydrogenation; Sn softens the Pt-ST bond without softening the Pt-EB interaction. As a result, oxidation catalysts abates unwanted byproducts and enhances the selectivity toward ST.

Further studies over Pt–Sn bimetallic catalysts by Zhu [54] and Late et al. [55], proved that Pt–Sn bimetallic catalysts are selective and stable in propane dehydrogenation reaction. In addition, there were other reports that Sn as an additive for Pt/ γ - Al_2O_3 catalysts improved the selectivity and stability of the catalyst in light alkane dehydrogenation reactions. Pham and co-workers stated in their study that the drawback to light paraffin dehydrogenation processes is coking, which deactivates the catalyst (Pt/ γ - Al_2O_3) and reduces the selectivity toward olefins. They proved that carbon deposits are not responsible for low catalytic performance, but the transformation of subnanometer Pt species into larger Pt nanoparticles. The solution by this group was addition of Sn to alumina which remains atomically dispersed and assist to redispersion of Pt on alumina and thereby improves catalytic performance [52]. Moreover, an experiment was conducted for the oxidative dehydrogenation of ethane to compare the catalytic activity of two catalysts, namely LaMnO_3 and 0.1%Pt0.2%Sn. The results revealed in the temperature interval of 600–900 °C and at $\text{C}_2\text{H}_6/\text{O}_2/\text{H}_2 = 4/1/2$ that the two catalysts had roughly the same ethane and oxygen conversion at all temperatures, but the selectivity to ethene was much higher over the Pt–Sn catalyst [56]. Considering these firm reports of well performance of Sn and Pt in the structure of catalysts for light alkanes dehydrogenation, it is quite predictable that in the dehydrogenation as well as oxidation of ethylbenzene, Pt and Sn in the structure of oxidation catalyst played a critical role as not only a selective catalyst toward production of ST (> 91%) but also as a stable catalyst at 873 K.

4 Conclusion

The primary purpose of this work was to select one of the catalysts (with the lowest performance) that had previously synthesized and tested in oxidative dehydrogenation of ethylbenzene and to improve its catalytic performance. Therefore, 5F/NCS selected and tested in a double-bed reactor with the help of the second catalyst (oxidation catalyst) that was obtained from Tabriz Petrochemical Company. Based on the GC analysis for both

catalytic tests, it was confirmed that oxidation catalyst has a profound impact on reducing the amount of side-products (benzene and toluene). On the other hand, oxidation catalyst enhanced styrene selectivity by further elimination of hydrogen. Based on previous literature, the presence of Sn and Pt elements in the structure of oxidation catalyst improved selectivity towards styrene. Sn softens the Pt-ST bond without softening the Pt-EB interaction leading to suppression of undesired byproducts and increasing styrene production. Considering the beneficial aspect of dehydrogenation and oxidation catalysts together in a double-bed reactor on one side, and economic factor for commercialization from another side, the further investigations are yet to come.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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