

INNOVATIVE PRODUCTION PROCESS OF STYRENE

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ABSTRACT

Composite catalysts for the oxidative dehydrogenation of ethylbenzene to styrene were synthesized based on zirconium, magnesium and aluminum oxide. Under the reaction conditions of $WHSV=0.5h^{-1}$, $EB : air = 1:6$ or $EB : CO_2 = 1:5$, $480^{\circ}C$, in the presence of O_2 , the conversion of EB and selectivity of St on $1\%ZrO_2, 2.0\%MgO/Al_2O_3 + 5\% P_2O_5$ catalyst reaches 62 and 90%, and in the presence of CO_2 , these indicators reach 54 and 94%, respectively. The inclusion of copper in the synthesized catalysts increases their activity and selectivity. The conversion of EB in the presence of CO_2 over $1\%ZrO_2, 2.0\%MgO/Al_2O_3 + 5\%P_2O_5 + 1\% CuO$ under reaction conditions of $WHSV = 1h^{-1}$, $GHSV = 500h^{-1}$, $500^{\circ}C$ is 62% and St selectivity is 96%. The inclusion of copper in the composition of the synthesized catalysts allows the conjugation of the dehydrogenation of EB to St with the steam conversion of carbon monoxide. The conjugation of these reactions increases the conversion of EB to St. In this case, under the reaction conditions of $500^{\circ}C$, $WHSV=0.5h^{-1}$, $GSHV = 500h^{-1}$, the conversion of EB is 65%, the St selectivity is 92 % on $1.0\%ZrO_2, 2.0\%MgO/Al_2O_3 + 5\%P_2O_5 + 1\%CuO$ catalyst. It was determined that the conjugation of the dehydrogenation of EB to St with the steam conversion of carbon monoxide allows to create a simultaneous and environmentally harmless process of obtaining styrene and hydrogen.

Keywords: ethylbenzene, oxidative dehydrogenation, styrene, steam conversion, carbon dioxide, carbon monoxide, conjugated reactions, environmentally friendly production.

Introduction

Catalytic transformations of hydrocarbons are usually accompanied by side reactions leading to the formation of undesirable products. The elimination of the such shortcomings associated with catalytic processes is an urgent problem in chemistry. Innovative solutions to such problems can be the involvement of the resulting undesirable by-products of industrial processes in conjugated reactions of their disposal, without affecting the main process.

At the moment, there are some industrial processes that have such shortcomings and they need to be renewed. One of the largest industrial processes in need of renewal is the production of styrene. Styrene is an important monomer for the synthesis of polymeric materials based on it, the production of which is steadily increasing. The main industrial process for the production of St is direct, energy-intensive dehydrogenation of EB. Since this process is a high-temperature, equilibrium-limited process, in order to lower the partial pressure of EB as much as possible, it is diluted with steam heated to $700-800^{\circ}C$ [1-4]. Steam dilution of EB has several advantages. Steam itself does not participate in the dehydrogenation reaction and acts as a diluent, shifting the equilibrium towards the conversion of ethylbenzene, providing part of the heat needed for

dehydrogenation, which is an endothermic reaction, reducing carbon deposits through the steam reforming reaction - preventing deactivation due to coke formation, by controlling the valence state of iron, i.e. limiting it to Fe_3O_4 under reaction conditions, it protects the catalyst from reduction to the metallic state - from overreduction and, therefore, from deactivation. However, the process of dehydrogenation of ethylbenzene with the presence of water vapor has important shortcomings. Thus, the dehydrogenation of EB to styrene is limited by equilibrium and is a highly endothermic reaction ($\Delta H_{0298\text{K}} = 28.1 \text{ kcal/mol}$ or $\Delta H_{0873\text{K}} = 125 \text{ kC/mol}$) [5-8]. Due to the endothermic nature of the reaction and the use of excess superheated water vapor, the industrial process consumes a lot of energy. Reducing the cost of production of St is possible by transferring the process from direct dehydrogenation of EB to oxidative one using CO_2 as an oxidizing agent [9-11]. In this case, the formation of St will be accompanied by an equivalent consumption of "specially prepared" CO_2 and the formation of an appropriate amount of carbon monoxide requiring utilization [12-14]. The noted drawbacks can be eliminated by involving the byproducts in conjugated reactions in a single reaction space. In the case of the oxidative conversion of EB to St with the participation of CO_2 , such a conjugated reaction can be the additional oxidation of carbon monoxide to dioxide by steam reforming. Carrying out such reactions is possible with the participation of composite catalytic systems, the components of which can be known catalysts of the main reaction and known catalysts of conjugated reaction.

The development of such processes with the participation of composite catalytic systems is very promising, but practically insufficiently studied and requires systematic research. Establishing the foundations for the use of the noted conjugated reactions for the implementation of such large-scale productions as the production of St is important not only for simplifying and intensifying these processes or eliminating their negative impact on the environment, but also for eliminating similar shortcomings in other industries.

The purpose of this work is to study the conjugation of dehydrogenation of ethylbenzene to styrene with steam conversion of carbon monoxide.

The experimental part

To study the conjugation of oxidative dehydrogenation of ethylbenzene to styrene with steam conversion of carbon monoxide, catalysts based on zirconium, magnesium, aluminum and copper oxide were synthesized.

$\text{MgO}/\text{Al}_2\text{O}_3$, $\text{ZrO}_2/\text{Al}_2\text{O}_3$ and $\text{ZrO}_2,\text{MgO}/\text{Al}_2\text{O}_3$ catalysts were prepared by impregnation of the corresponding metal salt solution in water into $\gamma\text{-Al}_2\text{O}_3$, dried at $120\text{-}150^\circ\text{C}$, calcined at 550°C and subsequent thermal calcining. $\text{ZrO}_2,\text{MgO}/\text{Al}_2\text{O}_3$ catalysts were prepared by two methods: sequential and co-impregnation methods.

A part of prepared $\text{ZrO}_2,\text{MgO}/\text{Al}_2\text{O}_3$ catalyst samples was treated with orthophosphoric acid. For this purpose, after keeping them in orthophosphate acid solution for 24 hours, the water phase was evaporated, the obtained extrudates were dried at $80\text{-}120$ and 300°C for 3 hours and calcined at $500\text{-}600^\circ\text{C}$. The amount of phosphorus in the samples is 5% (based on P_2O_5).

Taking some of the synthesized $1.0\%\text{ZrO}_2,2.0\%\text{MgO}/\text{Al}_2\text{O}_3$ sample, the $\text{ZrO}_2,\text{MgO}/\text{Al}_2\text{O}_3+\text{P}_2\text{O}_5+\text{CuO}$ catalysts were prepared on its basis. The $\text{ZrO}_2,\text{MgO}/\text{Al}_2\text{O}_3$ sample is impregnated with copper 2-nitrate solution of a certain concentration and is treated with ammonium carbonate, dried, washed, filtered through filter paper and kept in orthophosphoric acid for 24 hours. It is then evaporated. The obtained mass is dried at $80\text{-}120$ and 300°C for three hours and calcined at $500\text{-}600^\circ\text{C}$. In the finished sample, the amount of copper (according to

CuO) is 1 wt.%, and that of phosphorus is 5 wt.% (according to P₂O₅).

The experiments were performed in a flow-type catalytic unit equipped with a quartz reactor with a stationary catalyst bed.

The reaction products were analyzed by gas chromatography.

Conversion, yield and selectivity were calculated based on the initial amount of the components in the reactant and remaining in the catalysate.

Results and their discussion

Oxidative dehydrogenation of ethylbenzene to St on MgO/Al₂O₃, ZrO₂/Al₂O₃ and ZrO₂,MgO/Al₂O₃ catalysts.

For comparison, the activity of the synthesized catalysts in the oxidative dehydrogenation of ethylbenzene to styrene in the presence of atmospheric oxygen was first studied. The results of these studies are given below.

The primary aluminum oxide used in the preparation of catalysts is γ -Al₂O₃ with a specific surface area of 200 m²/g. Experiments show that this oxide is not very active in the oxidative dehydrogenation of EB. The activity of the catalysts for the oxidative dehydrogenation of ethylbenzene to styrene increases due to the effect of Mg, Zr (basic) oxides.

Impregnation of up to 2% MgO on alumina practically does not affect its activity, increasing the amount of MgO from 2% to 4% leads to EB conversion of 61.2 and selectivity to styrene to 90% . A further increase in the amount of MgO leads to a decrease in both activity and selectivity.

In case of impregnation of ZrO₂ on aluminum oxide, with the increase of ZrO₂ content from 0.4% to 2.0%, the activity of the samples increases up to 63.5% (ZrO₂ content is 1.3%) and then decreases. The selectivity of the conversion of ethylbenzene to styrene also increases monotonically from 86.3% to 91.5% with increasing ZrO₂ content from 0.4% to 1.3% and then decreases.

It is of interest to study the activity of the catalysts synthesized by joint impregnation of MgO and ZrO₂ on γ -Al₂O₃ in the oxidative dehydrogenation of EB to St. The results of the oxidative dehydrogenation of EB to styrene in the presence of oxygen on MgO/Al₂O₃ catalysts modified with 0.4% ZrO₂ show that the introduction of ZrO₂ into the catalyst under conditions standard for aluminomagnesium catalysts (500^oC, table 1) changes their catalytic properties. This change is not unequivocal.

Table 1. Conversion of EB to styrene over ZrO₂,MgO/Al₂O₃ catalysts WSHV=0.5 h⁻¹; T = 500^oC; EB:air = 1:6 (mol/mol)

MgO, %	ZrO ₂ , %	Conversion, %	St yield, mol%	ZrO ₂ , %	MgO, %	Conversion, %	St yield, mol%
4.0	0.0	61.2	50.4	1.3	0.0	63.5	58.1
2.0	0.4	63.0	52.1	0.4	2.0	55.7	50.1
4.0	0.4	60.5	49.3	0.7	2.0	60.2	54.8
6.0	0.4	59.5	48.5	1.0	2.0	63.5	58.4
8.0	0.4	57.4	42.3	1.3	2.0	60.2	51.2
10	0.4	40.4	32.9	2.0	2.0	53.6	44.5

Comparing the catalytic properties of ZrO₂, MgO/Al₂O₃ catalysts with MgO/Al₂O₃, it can be seen that the activity of ZrO₂, MgO/Al₂O₃ samples depends only on the amount of MgO. When

the amount of MgO in Al₂O₃ is increased to 2.0%, the introduction of ZrO₂ allows both the increase of the activity of the sample and the increase of the yield of St. A further increase in the amount of MgO decreases the activity of the catalyst. If we compare the conversion of EB and the yield of St at 500⁰C, we can see that a small change in the activity of the sample (57.5% instead of 63.0%) has little effect on the selectivity of St formation (84 % and 82.6%).

Incorporation of 0.4 % ZrO₂ into MgO/Al₂O₃ samples with large amounts of MgO led to a sharper decrease in activity than into samples with small amounts of MgO. To clarify this fact, the effect of MgO inclusion in the ZrO₂/Al₂O₃ sample on the activity of this sample in the oxidation of EB to St was investigated (table 1).

It can be seen from table 1 that the inclusion of MgO in ZrO₂/Al₂O₃ samples does not have an unambiguous effect on the oxidative dehydrogenation of EB to St. In contrast to the ZrO₂/Al₂O₃ samples, whose activities increase as the content of ZrO₂ increases up to 1.3%, the addition of 2.0% MgO leads to an increase in the activity of the ZrO₂/Al₂O₃ samples with only up to 1.0% ZrO₂. In samples with ZrO₂ content above 1%, addition of 2.0% MgO results in decreased activity.

Modification of ZrO₂/Al₂O₃ samples with MgO, as well as of MgO/Al₂O₃ samples with ZrO₂, allows lowering the reaction temperature to 475-480⁰C. At this time, the target product selectivity increases to 94% (1.0% ZrO₂, 2.0% MgO /Al₂O₃).

Thus, the study of the effect of the sequence of inclusion of activating ZrO₂ and MgO components shows that the sequence of inclusion of these components does not significantly affect the catalytic properties of ZrO₂, MgO/Al₂O₃ samples in the conversion of EB to St. The activity of these samples is probably limited by the total amount of activating components and the ratio of their amounts to each other.

A characteristic feature of the formation of St is the development of the activity of the catalyst during the course of the reaction, which ends in about 1 hour. Another feature of the primary catalyst is that it is not stable in the studied reaction. As can be seen from fig. 1a, the catalyst reaches the maximum yield of St and loses its activity after operating at this yield for some time (~1 h).

The effect of orthophosphoric acid modification on the activity of 1.0% ZrO₂, 2.0%MgO/Al₂O₃ catalyst was studied and the results are shown in figure 1 b. It was found that the maximum activity of the sample in the conversion of EB (63.5%) and the maximum yield of St (58.4%) (at 500⁰C) did not change even after treatment with orthophosphoric acid. It can be seen from the figure that the modification with orthophosphoric acid does not eliminate the effect of the development of the activity of the sample, but only slightly accelerates this process (the initial yield of styrene is 52% instead of 44% at 15 minutes). The possible importance of the modification with orthophosphoric acid is the increase in the stability of the catalyst. The results depicted in figure 1 b show that the activity of the orthophosphoric acid-modified sample does not decrease even after 5 h of working over the development period, and the yield of St is distinguished by its high selectivity achieved after the visible development of the catalyst activity (2 h) (Fig.1b).

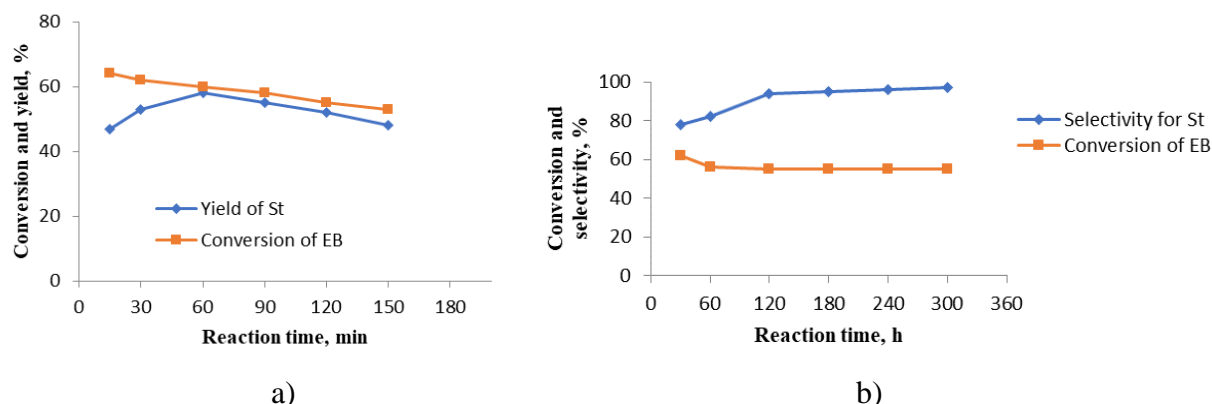


Figure 1. Dependence of the activity of 1.0%ZrO₂,2.0%MgO /Al₂O₃ (a) and 1.0%ZrO₂,2.0%MgO/Al₂O₃ + 5%P₂O₅ (b) catalysts in the oxidative dehydrogenation of EB to St from reaction time. WHSV = 0.5 h⁻¹, 480⁰C, EB : air = 1 : 6 (mole ratio).

Oxidative dehydrogenation of EB to St in the presence of CO₂ over 1%ZrO₂,2.0%MgO/Al₂O₃ catalysts.

The results of the study of the conversion of EB to styrene on zirconium-magnesium-aluminum oxide catalysts in the presence of CO₂ showed that the conversion of EB to St on these catalysts significantly depends on the ratio of CO₂ :EB (mol/mol). By increasing this ratio to 4-5 on 1.0%MgO, 2.0%ZrO₂/Al₂O₃, the conversion of EB increases to 53-54%, and the selectivity St reaches 94%. On the 1.0%ZrO₂, 2.0%MgO/Al₂O₃+5%P₂O₅ catalyst within the ratio of EB : CO₂ = 1 : 5 (mol/mol), the conversion of EB increases 2.5 times compared to conventional dehydrogenation, and the yield of St reaches 46%. A further increase in the EB : CO₂ ratio from 5 to 10 does not significantly affect the conversion of EB and the yield of St. Modification with orthophosphoric acid does not significantly affect the conversion and selectivity (conversion decreases by 3-4%, and selectivity decreases by 2%) (figure 2), and also increases the stability of the catalyst, as in the case of conversion in the presence of oxygen.

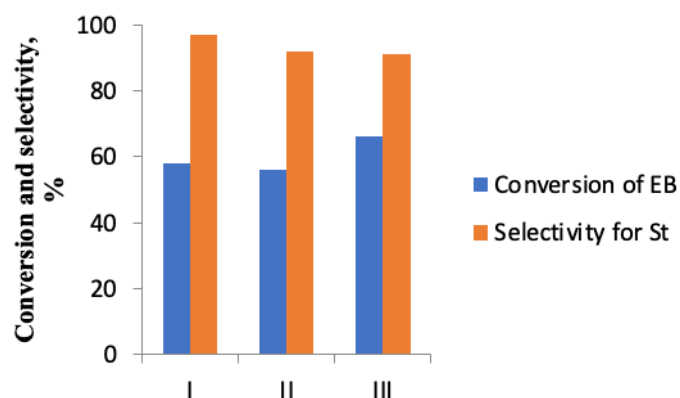


Figure 2. Conversion of EB to styrene in the presence of CO₂ over zirconium-magnesium-alumina catalysts. T=500⁰C; WHSV=1h⁻¹, GHSV=500h⁻¹; CO₂:EB=4:1 mol /mol. τ = 2 h.

I– 1.0%ZrO₂,2.0%MgO/Al₂O₃; II-1.0% ZrO₂,2.0%MgO/Al₂O₃ + 5.0% P₂O₅;
 III-1.0%MgO,2.0%ZrO₂/Al₂O₃ + 5.0% P₂O₅ +1%CuO

Promotion of 1.0%ZrO₂,2.0%MgO/Al₂O₃ catalyst treated with orthophosphoric acid with copper oxide leads to a further increase in the conversion of EB, already at the ratio of CO₂ : EB = 4 (mol/mol), the activity of the catalyst in the conversion of EB reaches 64% , but at this time the selectivity for St decreases slightly to 91% (figure 2).

Thus, under the influence of CO₂ on all three catalysts, the dehydrogenation of EB and the yield of St are increased compared to conventional dehydrogenation.

Catalytic activity of ZrO₂, MgO/Al₂O₃ catalysts in steam conversion of carbon monoxide.

To conjugate the dehydrogenation of ethylbenzene to styrene with steam conversion of carbon monoxide, the catalyst must have the ability to carry out steam conversion. Therefore, in the following experiments, the steam conversion of carbon monoxide on the synthesized catalysts was studied. The study of the conversion of CO on the 1.0%ZrO₂,2.0% MgO/Al₂O₃ catalyst shows that this compound does not undergo conversion. However, upon contact with CO, the catalyst turns black. Such a change in the color of the catalyst (turning from white to black) indicates that it is coking. The deposition of coke on the catalyst indicates that the Boudouard reaction is taking place on it:



This reaction takes place in the active centers of the studied catalyst, and the coke formed surrounds such centers and deactivates the sample, preventing the further course of the reaction. Carrying out a similar process with a mixture of CO:H₂O, when the ratio of the components of the mixture is changed from 1 to 2.5, shows that at 400 to 500°C steam conversion of carbon monoxide i.e. reaction (2) not gone:



However, in addition, under these conditions, coking of the catalyst is observed, which can be explained by the departure of the Boudouard reaction. However, raising the temperature to 600°C allows reaction (2) to proceed over the 1.0%ZrO₂,2.0%MgO/Al₂O₃ catalyst. The conversion of CO reaches 20% with the selective formation of H₂.

Modification of 1.0%ZrO₂,2.0%MgO/Al₂O₃ catalyst with orthophosphoric acid and copper significantly affects its activity. Thus, the comparison of the conversion of CO:H₂O mixture on 1.0%ZrO₂, 2.0%MgO/Al₂O₃ and 1.0%ZrO₂, 2.0%MgO/Al₂O₃+5%P₂O₅+1%CuO catalysts shows that the results differ. If the conversion of CO over 1.0%ZrO₂,2.0%MgO/Al₂O₃+5%P₂O₅+1%CuO catalyst at 500°C does not differ from the conversion over 1.0%ZrO₂,2.0%MgO /Al₂O₃, the introduction of H₂O molecules into the reaction at 500°C, activates reaction (2) on 1.0%ZrO₂,2.0%MgO/Al₂O₃ +5%P₂O₅+1% CuO (table 2).

Table 2. Effect of water vapor on carbon monoxide conversion on 1.0%ZrO₂,2.0%MgO/Al₂O₃ + 5%P₂O₅ +1%CuO catalyst. T = 500°C; GHSV = 500h⁻¹

H ₂ O:CO, mol	Conversion of CO,%	τ*,min	Yield of H ₂ , mol	(CO ₂ +H ₂) selectivity, %
0	trace	-	-	-
0.25	11	15	0.029	26
0.5	18	40	0.07	38
1.0	37	55	0.17	48
2.0	43	20	0.4	93
2.5	43	120	0.41	96

* stable working time of the catalyst

Depending on the composition of the H₂O:CO mixture, the conversion of CO can be raised above 40%, and as the ratio of H₂O : CO increases, the stability of the catalyst also increases (table 2).

The study of the conversion of the H₂O:CO mixture by additionally replacing carbon monoxide with synthesis gas (CO:H₂ = 1:2) shows that hydrogen, a direct conversion product of carbon monoxide, does not affect the process, that is, it does not slow down the reaction (Fig. 3).

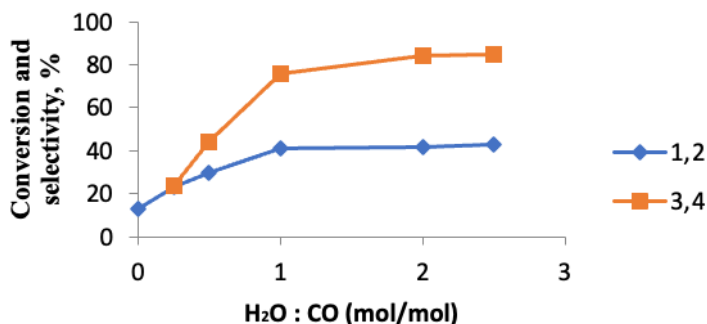


Figure 3. The effect of hydrogen on the conversion of carbon monoxide with water vapor. T = 500°C; GHSV = 500h⁻¹. 1,2- CO conversion, 3,4 selectivity. 1 and 3-CO + H₂O; 2 and 4-(CO + H₂) + H₂O).

Conjugation of conversion of EB to St with steam conversion of carbon monoxide on ZrO₂,MgO/Al₂O₃ catalysts.

The results of the study of the conjugation of conversion of EB to St with the steam conversion of carbon monoxide on 1.0%ZrO₂,2.0%MgO/Al₂O₃ catalysts showed that carbon monoxide itself does not affect the conversion of EB. However, it should be noted that coking deactivates the catalyst due to the Bouduar reaction. Conjugating the conversion of EB with the steam conversion of carbon monoxide increases the conversion of EB and the yield of St. Analysis of starting materials and reaction products shows that the conversion of carbon monoxide is very small, up to 8%. This, in turn, shows that the studied reactions are somewhat dependent on each other. The increase in EB conversion and selectivity to St in the presence of H₂O:CO mixture is undoubtedly due to the shift of the reaction towards the production of products, which leads to the idea of effective removal of the formed hydrogen from the reaction zone. Taking into account the low oxidizing capacity of CO, it can be assumed that either CO₂, a product of steam conversion of carbon monoxide, or its intense hydridation to methane is the basis of the interaction (combination) of reactions. However, it was shown above that hydrogen does not affect the conversion of carbon monoxide with water vapor. Therefore, the effect of the matching process on the conversion of EB to St is negligible. Treatment of 1.0%ZrO₂,2.0%MgO/Al₂O₃ sample with orthophosphoric acid and promotion with CuO leads to increase of EB conversion and selectivity to St in the presence of H₂O:CO mixture. As can be seen from figure 5, as the conversion of carbon monoxide increases in this catalyst, the conversion of EB and the selectivity to St also increase. At the same time, it should be noted that treatment of the 1.0%ZrO₂,2.0%MgO/Al₂O₃ sample with orthophosphoric acid reduces the development time of the catalyst activity. If we take into account that the development of activity of catalysts of the dehydrogelation process is explained by the formation of CP on the surface of

the catalysts, then the effect of phosphoric acid can be limited only by accelerating the accumulation of CP, the formation of which occurs with the participation of acid centers. Therefore, the increase of the activity of the catalyst in the target reaction is not only due to the accumulation of disproportionation products of carbon monoxide, which is facilitated (activated) due to the modification of the catalyst with CP, but most probably due to the activation of the conversion of carbon monoxide with water vapor of CuO. Common to both cases is the accumulation of CO₂. Thus, CO₂, the product of the conversion reaction of carbon monoxide with water vapor, is a possible source of the observed change in the conversion of EB to St.

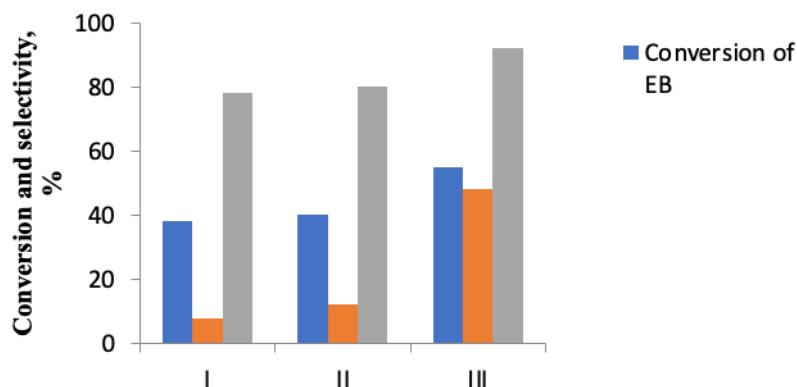


Figure 4. Conversion of EB to styrene in the presence of H₂O : CO. T=500⁰C; WHSV_{EB}=0.5 h⁻¹, GHSV_{H₂O:CO} = 500 h⁻¹, H₂O:CO = 2.5.

I – 1.0%ZrO₂,2.0%MgO/Al₂O₃;

II – 1.0%ZrO₂,2.0%MgO/Al₂O₃+5% P₂O₅;

III – 1.0%ZrO₂,2.0%MgO/Al₂O₃ + 1%CuO.

These results show that the oxidative dehydrogenation of ethylbenzene to styrene in the presence of CO₂ can be conjugated with steam reforming of the resulting carbon monoxide. Thus, the CO generated during the process can be converted into the oxidizing agent -CO₂ in the process itself and thus environmentally friendly St can be obtained.

Oxidative conversion of ethylbenzene is naturally accompanied by the formation and accumulation of oxidative condensation products (OCP), resulting in the development of low activity catalyst activity. It is believed that in the initial unstable stage of the process, St is formed in Lewis acid centers, then OCP is formed in the presence of these centers and oxygen. OCP is responsible for the oxidative dehydrogenation of EB. Accumulation of OCP until a monolayer is formed is the beginning of steady-state operation of the catalyst. A possible reason for the catalytic activity of OCP may be the geometric compatibility between EB and the centers located on the surface of OCP. As a result, there is a high concentration of carbon-oxygen centers responsible for the formation of St on the surface. Furthermore, the oxygen contained in the surface oxygenated groups is believed to be active enough to participate in the oxidative dehydrogenation of EB to St. Such a scheme does not involve EB forming any intermediate with oxygen. Therefore, the condensation products (CP) formed before the formation of OCP in oxidative conversion are the same as the CP formed during the direct dehydrogenation of EB. From this point of view, it can be assumed that similar forms of OCP are formed from the interaction of CO₂ with the previously formed CP as a result of the usual dehydrogenation of EB.

Thus, the following scheme of the formation of active centers in CP with the participation of O₂ and CO₂ in the conversion of EB to St can be proposed:



where C are carbon defects in CP; [O...CO-C] [O...CO... C] shows the interaction of CO₂ with carbon centers (defects) in CP and its dissociation into oxygen atom and CO.

Thus, the results of the studies showed that an innovative process for the production of styrene can be implemented, which is environmentally friendly and allows significant savings in capital investments through the use of atmospheric oxygen, carbon dioxide and conjugating the dehydrogenation of ethylbenzene into styrene with steam conversion of carbon monoxide.

References

1. Hanqing, G.E., Wenchao, Y.I.N., Guoqing, Y.A.N.G.: Review on vanadium oxide catalysts for oxidative dehydrogenation of ethylbenzene with CO₂. Chemical industry and engineering progress. 102,1868-1882 (2021). doi: 10.16085/j.issn.1000-6613.2020-1975
2. Jiang, N., Burri, A., Park, S.E.: Ethylbenzene to styrene over ZrO₂-based mixed metal oxide catalysts with CO₂ as soft oxidant. Chinese Journal of Catalysis. 37, 3–15 (2016). doi: 10.1016/S1872-2067(15)60901-9
3. Kai, R.J., Jin, S., Yong, H.: Catalytic behavior of manganese oxides for oxidative dehydrogenation of ethylbenzene with carbon dioxide. Journal of CO₂ Utilization. 22, 63–70 (2017). doi: 10.1016/j.jcou.2017.09.011
4. Christian, N., Valeriya, Z., Ignacio, V. Application of staged O₂ feeding in the oxidative dehydrogenation of ethylbenzene to styrene over Al₂O₃ and P₂O₅/SiO₂ catalysts. Applied Catalysis A: General. 476, 204–214 (2014). doi: 10.1016/j.apcata.2014.03.002
5. Liu, W., Wang, C., Su, D.: Oxidative dehydrogenation of ethylbenzene on nanocarbon: Kinetics and reaction mechanism. Journal of Catalysis. 368, 1-7 (2018). doi: 10.1016/j.jcat.2018.09.023
6. Tehua, W., Siying, C., Tongtong, W.: The physicochemical properties and catalytic performance of carbon-covered alumina for oxidative dehydrogenation of ethylbenzene with CO₂. Applied Surface Science. 427, 1011 – 1018 (2018). 10.1016/j.apsusc.2017.08.139
7. Itika, K., Gurram, V.R.B., Jayesh, T.B.: Development of stable MoO₃/TiO₂-Al₂O₃ catalyst for oxidative dehydrogenation of ethylbenzene to styrene using CO₂ as soft oxidant. Journal of CO₂ Utilization. 18, 309 – 317 (2017). doi:10.1016/j.jcou.2017.02.010
8. Venkata, R.M., Velpula, V., Thirupathiah, K. Oxidative dehydrogenation of ethylbenzene over γ-Al₂O₃ supported ceria-lanthanum oxide catalysts. Arabian Journal of Chemistry. 13, 772-782 (2020). doi:10.1016/j.arabjc.2017.07.014
9. Venkata, R.M., Peddinti, N., Challa, P.: La₂O₃ promotional effect to Co₃O₄/γ-Al₂O₃ catalyst in the oxidative dehydrogenation of ethylbenzene with CO₂ as soft oxidant. Journal of Saudi Chemical Society. 23, 678-690 (2019). doi:10.1016/j.jscs.2018.10.001
10. Tagiev, D.B., Gasimov, G.O., Rustamov, M.İ.: Carbon deposits on the surface of CaO/SiO₂ as active catalysts for the oxidative dehydrogenation of ethylbenzene. Catalysis Today. 102, 197 – 202 (2005). doi: 10.1016/j.cattod.2005.02.001

11. Borges, M. C., Barbosa, F.F., Morales, M. A.: Oxidative dehydrogenation of ethylbenzene to styrene over the CoFe_2O_4 -MCM-41 catalyst: preferential adsorption on the $\text{O}^{2-}\text{Fe}^{3+}\text{O}^{2-}$ sites located at octahedral positions. *Catalysis Sciences Technology*. 9, 2469–2484 (2019). doi:10.1039/C9CY00618D
12. Zhang, N., Zhang Y., Li, X.: Ketone-group containing condensed organic molecules supported on SBA-15 for the oxidative dehydrogenation of ethylbenzene to styrene. *Molecular Catalysis*. 517, 112-118 (2022). doi:10.1016/j.mcat.2021.112018
13. Zhiying, L., Yulin, L., Xiaohui, S.: Superior performance of $\text{K/Co}_2\text{AlO}_4$ catalysts for the oxidativedehydrogenation of ethylbenzene to styrene with N_2O as an oxidant. *Journal of Industrial and Engineering Chemistry*. 112, 67-75 (2022). doi:10.1016/j.jiec.2022.04.036
14. Mariana, G. C., Alain, F.K., Michel, M.R.: Inhaled anesthetics: environmental role, occupational risk, and clinical use. *Journal of Clinical Medicine*. 10, 2-22 (2021). doi: 10.3390/jcm10061306

STIROLUN İNNOVATİV İSTEHSAL PROSESİ

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Xülasə. Etilbenzolun stirola oksidləşdirici dehidrogenləşməsi üçün sirkonium, maqnezium və alüminium oksidləri əsasında kompozisiya tərkibli katalizatorlar sintez edilmişdir. $\text{WHSV}=0.5\text{h}^{-1}$, $\text{EB} : \text{hava} = 1:6$ və ya $\text{EB} : \text{CO}_2 = 1:5$ (mol/mol), 480°C reaksiya şəraitində, $1\%\text{ZrO}_2, 2\%\text{MgO/Al}_2\text{O}_3 + 5\%\text{P}_2\text{O}_5$ katalizatoru üzərində O_2 -nin iştirakı ilə EB-nin çevrilməsi və St görə seçicilik, müvafiq olaraq, 62 və 90%-ə, CO_2 -nin iştirakı ilə isə bu göstəricilər 54 və 94%-ə çatır. Sintez edilən katalizatorlara misin daxil edilməsi onların aktivliyini və seçiciliyini artırır. $\text{WHSV}=1\text{h}^{-1}$, $\text{GHSV}=500\text{h}^{-1}$, 500°C reaksiya şəraitində $1\%\text{ZrO}_2, 2\%\text{MgO/Al}_2\text{O}_3 + 5\%\text{P}_2\text{O}_5 + 1\%\text{CuO}$ üzərində CO_2 -nin iştirakı ilə EB-nin çevrilməsi 62% və St görə seçicilik 96% təşkil edir. Sintez edilmiş katalizatorların tərkibinə misin daxil edilməsi dəm qazının buxar konversiyası ilə EB-nin St-a dehidrogenləşməsinin qoşulmasına imkan verir. Bu reaksiyaların qoşulması EB-nin St-a çevrilməsini artırır. Bu halda 500°C , $\text{WHSV}=0,5\text{h}^{-1}$, $\text{GSHV}=500\text{h}^{-1}$ reaksiya şəraitində $1\%\text{ZrO}_2, 2\%\text{MgO/Al}_2\text{O}_3 + 5\%\text{P}_2\text{O}_5 + 1\%\text{CuO}$ üzərində EB-nin çevrilməsi 65%, St görə seçicilik 92% təşkil edir. Müəyyən edilmişdir ki, EB-nin St-ə dehidrogenləşməsinin dəm qazının buxar konversiyası ilə qoşulması stirol və hidrogenin eyni vaxtda və ekoloji cəhətdən zərərsiz alınması prosesini yaratmağa imkan verir.

Açar sözlər: etilbenzol, oksidləşdirici dehidrogenləşmə, stirol, buxar konversiyası, karbon dioksid, karbon monooksid, qoşulmuş reaksiyalar, ekoloji təmiz istehsal

ИННОВАЦИОННЫЙ ПРОЦЕСС ПРОИЗВОДСТВА СТИРОЛА

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РЕЗЮМЕ

Синтезированы композиционные катализаторы окислительного дегидрирования этилбензола (ЭБ) в стирол (Ст) на основе оксидов циркония, магния и алюминия. На катализаторе 1%ZrO₂, 2% MgO/Al₂O₃+5% P₂O₅ в условиях реакции WHSV=0,5ч⁻¹, ЭБ:воздух = 1:6 или ЭБ:СО₂ = 1:5 (моль/моль), 480⁰С, в присутствии О₂ конверсия ЭБ и селективность по Ст достигает 62 и 90 %, а в присутствии СО₂ эти показатели достигают 54 и 94 %, соответственно. Включение меди в синтезированные катализаторы повышает их активность и селективность. Конверсия ЭБ в присутствии СО₂ на 1%ZrO₂, 2% MgO/Al₂O₃+5% P₂O₅+1%CuO в условиях реакции WHSV=1ч⁻¹, GHSV=500ч⁻¹, 500⁰С составляет 62%, а селективность по Ст-96%. Включение меди в состав синтезированных катализаторов позволяет сопрягать процесс дегидрирования ЭБ в Ст с паровой конверсией монооксида углерода. Сопряжение этих реакций увеличивает конверсию ЭБ в Ст. При этом на катализаторе 1,0%ZrO₂, 2% MgO/Al₂O₃+ 5% P₂O₅+1%CuO в условиях реакции 500⁰С, WHSV=0,5ч⁻¹, GSHV=500ч⁻¹ конверсия ЭБ составляет 65%, селективность по Ст - 92. %. Установлено, что сопряжение дегидрирования ЭБ в Ст с паровой конверсией монооксида углерода позволяет создать экологически безвредный процесс получения стирола и водорода.

Ключевые слова: этилбензол, окислительное дегидрирование, стирол, паровая конверсия, диоксид углерода, монооксид углерода, сопряженные реакции, экологически чистое производство.