UDC 547.534.1: 542.941.8

EFFECT OF CARBON DIOXIDE ON OXIDATIVE ETHYLBENZENE DEHYDROGENATION IN THE PRESENCE OF ALUMINUM-CHROMIUM CATALYSTS

M.T.Mamedova

Mammadaliyev Institute of Petrochemical Processes, NAS of Azerbaijan.

memmedova-melahet@mail.ru

Received 23.09.2020

Accepted 21.12.2020

In order to create a more efficient process for the production of styrene from ethylbenzene by selective oxidation of the resulting hydrogen, model aluminum-chromium catalysts with different modifier (Cu) contents were prepared, and O₂, CO₂ and a mixture of CO₂:air were used as an oxidant. It has been established that the process of obtaining of styrene from ethylbenzene on alumochromic catalysts is characterized by a high intensity. Alumochromic catalysts modified by Cu and promoted by 15 mass.% K₂CO₃ in the presence of carbon dioxide increase the conversion of ethylbenzene by 14%, and the selectivity of the formation of styrene by 10% as a result of the transferring dehydrogenation of compaction products to the products of oxidative compaction. The presence of oxygen in the oxidizing mixture CO₂:air blocks the participation of carbon dioxide in the selective oxidation of hydrogen isolating at the dehydrogenation of ethylbenzene. It has been established that the most selective alumochromic catalysts in the oxidative dehydrogenation of ethylbenzene to styrene contain 1.5–2.5 mass.% of the modifying component (Cu).

Keywords: ethylbenzene, styrene, oxidative dehydrogenation, model alumochromic catalysts, modification by copper, the oxidizing mixture of CO₂:air, CO₂, products of compaction, products of oxidative compaction.

doi

Introduction

Industrial processes based on dehydrogenation are accompanied by high energy costs. This, in its turn, limits the amount of the initial reagent, and therefore, industrial dehydrogenation processes are implemented at low volume rates (v.r.). For the dehydrogenation of ethylbenzene (EB) to styrene (St), the maximum space velocity (in liquid) does not exceed 0.5 h⁻¹ [1]. As a result, the production of styrene on an industrial scale requires the use of reactors a large capacity that, in turn, increases the material consumption of the process. Thus, the intensification of the process for the production of styrene from ethylbenzene with reduced energy and material costs is an urgent problem in petrochemistry and requires finding effective solutions to remove these shortcomings. The oxidative dehydrogenation of ethylbenzene to styrene by oxidizing the hydrogen isolated in this process is one of the possible solutions to the problems which arise, since in this case occurs an effective shift of the reaction towards styrene formation and ensuring the energy costs

of the reaction. With this important to note that the water molecules formed can promote the desorption of styrene product molecules from the catalyst surface and increase the selectivity of the process. In this regard, there is an intensive search for oxidants for the catalytic oxidation of EB in St. To the number of like oxidant - refers O₂, SO₂, N₂O, CO₂ [2–7]. The latter compound, as a mild oxidizing agent, is the subject of ever-expanding research. In 1991, Matsui and his colleagues first reported the positive effect of CO₂ in relation to deactivation of an industrial catalyst for the dehydrogenation of ethylbenzene to styrene [8]. After that, interest in the presence of CO₂ in the processes of hydrocarbon conversion has increased intensively [9, 10]. It was determined that in the reaction of converting EB to St, CO₂ acts as a diluent and oxidizing agent, shifts the equilibrium of EB conversion towards styrene formation, increases EB conversion, improves selectivity styrene [11], maintains the active phase of oxide catalysts in the required oxidation grade, provides better heat supply due to its high heat capacity,

suppresses undesirable deep oxidation products, removes coke from the catalyst surface by the reverse Boudoir reaction [12]. Bartholomew C.H. determined a number of oxidizing ability of various gases at coke gasification: O_2 (105) > H_2O (3) > CO_2 (1) > H_2 (0.003). The numbers in parentheses clearly indicate that CO_2 can be considered an oxidizing agent [13]. Typical characteristics of these gases were summarized in tabular form in a review by Park and Han [14]. According to these data, CO_2 has the highest heat capacity among other typical gases and, due to this, CO_2 prevents hot spots on the catalyst surface. Taking into account all these unique features, CO_2 can be considered as a mild oxidizing agent for use in the oxidative conversion of hydrocarbons [15].

One of the first studies on the use of CO_2 as a diluent and oxidizing agent in the dehydrogenation of EB in St was carried out by Sugino M.O. and co-workers. They used lithium promoted iron catalyst supported on activated carbon. At 500–700°C, the styrene yield reached 40–45% with a styrene selectivity of more than 90%. In addition to styrene, CO and water formed. This proved that the reaction proceeds according to the oxidative dehydrogenation mechanism [16].

The mechanism of conversion of EB to St in the presence of CO_2 and the role of the latter in this process are extensively discussed in the literature. Mimura and Saito showed that the conversion of EB to St in the presence of CO_2 onto an iron oxide catalyst supported on alumina proceeds in two ways: the one-step path by reaction 1 – the oxidative dehydrogenation of EB in the presence of oxygen formed from the dissociation of CO_2 and the two-step path by reaction 2 and 3 – first, the usual dehydrogenation of EB occurs by 2, and then the oxidation of the formed hydrogen with CO_2 to water (reverse reaction of the conversion of water gas and CO) (3) [17]; Ventaka R.M. and Kamaraju S.R.R. showed that the process on Co_3O_4/Al_2O_3 proceeds in a two-step way (equations 2 and 3) [18]; In [4], the authors suggest that the process on $KFePMo11W$ proceeds in a one-step way (1); Pak and Wislovsky [19], as well as Shuwei [12] showed that EB

dehydrogenation in the presence of CO_2 on $VSbOx/Al_2O_3$ and V_2O_5/SiO_2 catalysts, respectively, proceeds according to the redox mechanism, where oxidative dehydrogenation occurs due to lattice oxygen of the catalyst (equation 4 and 5):

here MO_x – metal oxide included in the catalyst composition.

As a result of investigation, carried out by disaffected scientists, it was found that the mechanism of conversion of EB to St in the presence of CO_2 depends on the nature of the catalyst.

Many researchers have compared the activity of catalysts in the presence of CO_2 and other oxidizing agents.

D. Gong and co-workers on comparing the activity of the $V_{0.43}Sb_{0.57}O_x/Al_2O_3$ catalyst in the presence of O_2 , N_2 , H_2O and CO_2 in the conversion of EB to St. [20] they found that the greatest yield of styrene and selectivity for styrene in the presence of CO_2 .

Based on the thermodynamic calculation, Mimura and Saito comparing the equilibrium yield of styrene in direct EB dehydrogenation in the presence of water vapor and in oxidative dehydrogenation in the presence of CO_2 revealed that at the same temperatures, the equilibrium yield of St in the presence of CO_2 rather higher. They estimating the energy costs of obtaining St from EB in the presence of CO_2 (commercial process) and showed that this cost is 6.3×10^8 kal/t·St and 1.5×10^8 kal/t·St respectively [17].

Javani F. and Trifiro F. proved that, in the presence of CO_2 , the dehydrogenation equilibrium of EB shifts toward styrene formation and leads to an increase in ethylbenzene conversion and styrene selectivity [21].

Since the 90s intensive research has been continuing on the search for optimal catalysts

for the oxidative dehydrogenation of EB in St in the presence of CO₂. Studies have shown that catalysts with an optimal balance of acid-base and redox properties, have high activity and selectivity for styrene [22] in the presence of CO₂. Oxides of some metals deposited on alumina; catalysts with of high activity in the reverse water-gas shift reaction, metal oxides supported on mesoporous materials are highly active in the conversion of EB to styrene in the presence of CO₂ [7, 19]. These studies found that the formation of carbon deposits on the surface of the catalysts during the reaction, usually lead to deactivation of the catalyst by coking. However, there exist are a number of cases where such deposits can improve catalytic properties. It was shown in [24–26] that carbon deposits, which initially form on the surface of catalysts, are responsible for the increased activity and selectivity of the reaction. However, increasing the amount of carbon deposits value more than the monolayer reduces the activity of the catalyst due to the loss of available surface area and oxygen groups (mainly the -C = O group) on these deposits. It is shown that defects and edges of carbon deposits play an important role in the reaction mechanism.

Despite the wide range of catalysts studied and the selection of various oxidizing agents that make it possible to subject EB to oxidative dehydrogenation in St, and the presence of such catalytic process parameters as achieving 100% EB conversion and 97.7% St selectivity at 380°C and a contact time of 3.6 sec [27], oxidative dehydrogenation of EB in St is still not industrially implemented. Therefore, new research is required related to the search for new, more stable catalytic systems, and clarification of the features of this reaction.

In this regard, we have synthesized several variants of catalysts and studied their activity in the oxidative dehydrogenation of ethylbenzene.

In the investigation we carried out earlier for the oxidative dehydrogenation of ethylbenzene to styrene based on γ -Al₂O₃, catalysts containing oxides of Mg, Zr and phosphorus, as well as mixtures of these modifiers, were pre-

pared [28]. It was established the activities of these samples depend on the amount and ratio of the components deposited, and the optimal values are 1.0% by mass of ZrO₂ and 2.0–4.0% by mass of MgO. The synthesized samples have a high activity in the oxidative dehydrogenation of ethylbenzene to styrene (EB conversion reaches 60% with a selectivity of 90%). The drowing of MgO and ZrO₂ on γ -Al₂O₃ separately and together contribute to a decrease in the process temperature by 20 and 50°C, respectively. The introduction of phosphorus into MgO and ZrO₂/Al₂O₃ catalysts helps to reduce the catalyst activation time and increases the stability of its operation. The development of the catalyst is accompanied by the accumulation of carbon deposits, leading to an increase in the yield of styrene, and further to a decrease in its activity.

The catalysts were synthesized based on the spent industrial aluminum-chromium catalyst used in the hydrocarbon dehydrogenation by SABIC Co., and the catalysts were modified with copper and potassium carbonate [29]. The catalysts were tested in the oxidative dehydrogenation of ethylbenzene to styrene. It was found that the prepared and modified 1 wt % Cu catalyst, upon the conversion of ethylbenzene to styrene in the presence of O₂, exhibits an activity of 53% with a selectivity for styrene of 85%. It was shown that the introduction of carbon dioxide into the reaction zone leads to an increase in activity to 60–63%, and selectivity to 89–91%. The stability of the functioning of a copper-promoted catalyst and the effect of water vapor on the process were studied. It was found that under conditions close to industrial, within 100 h, a stable conversion of the mixture (ethylbenzene:O₂ = 9:1):H₂O = 4:1 with a selectivity for styrene of at least 90% at a space velocity of 2 h⁻¹ (by liquid ethylbenzene).

Continuing the our work in the present study, we synthesized model aluminum-chromium catalysts modified with copper and promoted with potassium carbonate and studied their activity in the conversion of ethylbenzene to styrene in the presence of O₂, CO₂ and their mixture under conditions close to the conditions

for the industrial dehydrogenation of this hydrocarbon to St (600°C , atmospheric pressure, lowering the partial pressure of the hydrocarbon by dilution), but characterized by an increased volumetric rate of the reactant feed.

Experimental part

As an aluminum component in the synthesis of an aluminum-chromium catalyst, an industrial paste-like aluminum gel was used. The chromium component was implemented following from potassium bichromate. The initial potassium bichromate was thoroughly mixed with ammonium chloride and calcined at temperatures of $550\text{--}600^{\circ}\text{C}$. Ammonium bichromate formed as a result of the exchange decomposes to chromium(III) oxide. Obtained dark green mixture was washed with distilled water to remove potassium chloride, filtered, and then the precipitate was treated with a concentrated KOH solution. After vigorous stirring for 5 hours, the solution was diluted with distilled water and left overnight. After this, a gel-like precipitate formed was decanted, which was additionally dehydrated in air at room temperature for one day. Then, the paste-like gels of aluminum and chromium oxides were thoroughly mixed until a homogeneous consistent mass was obtained, which was extruded by passing it through a 3 mm diameter, dried under an electric incandescent lamp (24 hours), were crushed and placed into 5–6 mm cylinders, and dried at 80°C (3 h), 120°C (3 h), and stepwise raising the temperature ($100^{\circ}\text{C}/1.5$ h), calcined at 700°C for 3 hours.

The finished sample contained 30 mass.% Cr_2O_3 , the rest was Al_2O_3 . Part of the sample was promoted with potassium carbonate, keeping in solution of given concentration for 24 hours, and then evaporated and subjected to drying and calcination according to the method described above. The content of K_2CO_3 in the finished catalyst was 15%.

The rest of the sample was modified with copper, keeping the sample in a porcelain dish with a given concentration of copper nitrate solution (48 h). After that, the sample was dried and treated with saturated sodium hydrocar-

bonate solution, decanted with distilled water, dried at 80°C (3 h) and 120°C (3 h). The obtained samples were placed in a reactor and reduced in a stream of hydrogen at 185°C and the linear rate of hydrogen supply to the reactor was $20\text{ cm}^3/\text{min}$. The recovery process was continued until the complete release of water vapor in the trap placed at the outlet of the reactor. The copper-modified samples were further promoted with K_2CO_3 as described above.

The specific surface area of the catalysts was determined by benzene adsorption and calculated by the BET equation.

Ethylbenzene transformations were studied in a flow-type catalytic unit equipped with a quartz reactor with a catalyst loading of $3\text{--}10\text{ cm}^3$.

Before carrying out the experiments, the catalysts were subjected to standard processing: in a stream of air ($20\text{ cm}^3/\text{min}$), the temperature of the reactor was raised to 650°C and the sample was kept at this temperature for 1 h. Further, the temperature was lowered to 600°C , and after its stabilization ethylbenzene was introduced into the reactor by a liquid volume velocity of 2 h^{-1} , and air speed was regulated so as to adhere to the ratio of $\text{EB}:\text{O}_2 = 4:1$ ($25\text{ cm}^3/\text{min}$). Ethylbenzene was fed into the reactor by a mechanical syringe into the mixer-evaporator, where air also entered, and the reactants were mixed. It should be noted that the evaporator-mixer also served as a heater. The air used in the studied reaction was pre-humidified by moistened by bubbling through water at a temperature of 70°C .

CO_2 was supplied to the reactor from the gas meter by displacing it at a certain rate, controlled by the supply of a solution from a measuring tank ($20\text{--}40\text{ ml}/\text{min}$). Carbon dioxide also entered the evaporator-mixer, and then into the reactor as part of the mixture.

Gaseous and liquid products were analyzed simultaneously using an online GC (Younlin Instrument, Acme 6000 series, Korea) equipped with a katharometer and flame ionization detector. To analyze gaseous products (hydrogen, carbon monoxide, methane and carbon dioxide), a Poropak Q column ($1.83\text{ m}\times 3.2\text{ mm}$) was used, and liquid products were ana-

lyzed in a column (length 30 meters, inner diameter 0.32 mm) with Innowax (film thickness 0.25 μm).

Results and discussion

Preliminary studies of the conversion of EB were carried out in the absence of oxidizing agents. In order to maintain the hydrodynamic parameters of the process, the oxidizing agent was replaced with an inert gas (nitrogen), and the volumetric flow rate of the liquid was 0.5 h^{-1} . As can be seen from figure 1 *a* and *b* (curves 1 and 1'), at the initial moment of the reaction, a certain time interval is observed corresponding to the activation of the catalyst, the activity of which reaches 30% by 30 min of experiment and remains almost constant.

Analysis of the reaction products showed their composition: benzene – 14%, toluene – 4% and the target product styrene – 80%. The remaining unidentified products (~2–4%) are likely to be degradation products.

Carrying out the reaction in the presence of an oxidizing agent - oxygen of the air shows (Figure 1 *a* and *b*, cr. 2, 2') that the main laws of the conversion of ethylbenzene to styrene remain practically unchanged and selectivity by styrene remains at the level of 80%. At the same time, the introduction of oxygen into the process increases the degree of conversion of ethylbenzene, *ceteris paribus*, by almost 20%.

In this case, due to the action of the oxidizing agent, the volumetric rate of the process increased approximately four times (2 h^{-1} by liquid) and, consequently, the intensity of the process also increased.

The copper modification of the model catalyst has a significant effect on the conversion of ethylbenzene. From the data in Figure 1 *a* and *b* (curves 4 and 4') it is seen that in the presence of oxygen, modification with copper not only increases the degree of conversion of ethylbenzene, but also increases the selectivity for the target product by 4–6%. From the data in Figure 1 *a* and *b*, it also follows that during the dehydrogenation of ethylbenzene on a copper-modified aluminum-chromium catalyst without an oxidizing agent, curves 1 and 3; 1' and 3' almost coincide. This suggests that the modification of the aluminum chromium catalyst with copper does not affect the "pure" dehydrogenation ability of the model catalyst. Therefore, an increase in the activity and a shift in the reaction of dehydrogenation of ethylbenzene on an aluminum-chromium catalyst towards the formation of the target product may be associated with an increase in the ability of the catalyst to selectively oxidize the resulting hydrogen. An additional argument to this is the results of previous studies on the oxidative dehydrogenation of ethylbenzene on copper-

Fig. 1a and b. Dehydrogenation of ethylbenzene to styrene on model aluminum-chromium catalysts: $T = 600^{\circ}\text{C}$, $\text{WHSV} = 2 \text{ h}^{-1}$. $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ 15% K_2CO_3 - 1, 1' - non-oxidative dehydrogenation; 2, 2' - oxidative dehydrogenation; 1.5% Cu/ $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ + 15% K_2CO_3 - 3, 3' - non-oxidative dehydrogenation; 4, 4' - oxidative dehydrogenation 1, 2, 3, 4 - conversion; 1', 2', 3', 4' - selectivity.

aluminum catalysts [30]. By the results of these studies, the process proceeds only with a catalyst sample, the copper content of which is 25–30 mass.%. A sample containing 1.0–1.5 mass.% copper is not active in the process under study.

The replacement of oxygen by carbon dioxide during the oxidative dehydrogenation of ethylbenzene to styrene leads to a noticeable increase in the selectivity of the process for styrene (Table 1).

As noted above, of particular interest is the study of the conversion of EB to St in the presence of mixtures of two oxidizing agents: CO₂: air. These studies were carried out under the composition of the mixture components changed from zero to 100%. It has been established, that the yield of products and the overall conversion of EB depend on the ratio of the components of the oxidant.

The results obtained show (Figure 2) that with an increase in air concentration, above 40 vol. %, the activity of the catalyst increases,

reaching a limit value of 75%. With an air ratio of less than 40 vol. %, the activity of the catalyst increases again and, when using individual CO₂, reaches a limit value of 42%. It can be seen from the data in Figure 2 that the stabilized EB conversion (i.e., after the catalyst reaches a stationary level) has a complex dependence on the composition of the CO₂: air mixture and is characterized by the presence of a certain minimum value, within the ratio of CO₂: air = 3:2.

The complex nature of the dependence on the CO₂: air ratio is also observed for the selectivity of the formation of St. From the data in Figure 2 it can be seen that with an increase in the air content in the mixture used up to almost 80%, the selectivity (for St) of the oxidation process exceeds the similar selectivity of the catalyst in direct dehydrogenation of EB. At higher concentrations of oxygen (air) in a mixture with carbon dioxide, the selectivity of oxidative dehydrogenation decreases quite sharply to 62%.

Table 1. The effect of air and CO₂ on the conversion of ethylbenzene and the composition of the resulting hydrocarbon products. Catalyst - 1.5%Cu/Al₂O₃·Cr₂O₃ + 15% K₂CO₃; T = 600°C; τ = 2 h

Inert gas and oxydant	EB:Oxy.	WHSV, h ⁻¹	Conv. of EB, %	Select. for St, %	Hydrocarbon products, %				CD*, wt%
					CH ₄	C ₂	C ₆ H ₆	C ₇ H ₈	
Nitrogen	EB:N ₂	0.5	28	80	0.9	2.0	5.0	3.5	0.83
Air	EB:O ₂	2.0	75	62	6.0	3.0	3.0	2.5	0.92
CO ₂	EB:CO ₂	2.0	42	90	0.3	0.7	2.2	2.8	0.88

* – Accumulation of carbon deposits (CD) on the catalyst for 1 h.

Fig. 2. The dependence of the oxidative dehydrogenation of ethylbenzene to styrene on the composition of the oxidant CO₂: air. Catalyst – 1.5% Cu/Al₂O₃·Cr₂O₃ + 15% K₂CO₃; T = 600°C; WSHV = 2 h⁻¹, τ = 2 h.

From the data in Figure 2 also implies that under the influence of carbon dioxide, a selective oxidation of part of the formed hydrogen occurs. Due to this, the conversion of EB increases by 12% with approximately the same increase in selectivity for St. Taking into account that the yield of low molecular weight carbons C_1 – C_2 decreases by 14%, i.e. the contribution of hydrodealkylation is reduced in comparison with conventional dehydrogenation of EB, it can be assumed that part of the generated hydrogen is spent on interaction with CO_2 (reaction 3).

The effect of air on the EB transformation is characterized by a high conversion of the latter and a relatively low yield of St (selectivity $\approx 60\%$). In particular, with decreasing contact time, conversion decreases, and selectivity increases due to a reducing contribution of deeper EB oxidation. A similar effect is exerted by a decrease in the concentration of oxygen (air) in the oxidizing mixture used, leading to an increase in the selectivity of St formation (Figure 2). At the same time, the oxidative interaction of CO_2 with hydrogen formed as a result of dehydrogenation of EB is suppressed by oxygen. The observed decrease in catalyst activity can be explained by this fact.

Naturally, the process of oxidative dehydrogenation is accompanied by the formation and accumulation of products of oxidative compaction (POC) and, as a result of which, the development of a low-activity catalyst takes place [31, 32]. It is assumed that in the initial non-stationary stage of the process, St is formed at the Lewis acid centers and at POC, which is formed with the participation of these centers and oxygen. Responsible for oxidative dehydrogenation of EB is POC; its accumulation to a monolayer coating is the beginning of a steady-state mode of catalyst functioning [31]. A possible reason for the catalytic activity of POC may be a large geometric correspondence between its structure and structure EB, due to which on the surface are created high concentrations of carbon-oxygen centers responsible for the formation of St. Moreover, it is assumed that oxygen from oxygen-containing surface

groups is sufficiently reactive to participate in oxidative dehydrogenation of EB in St [31]. Such a scheme does not imply the formation of any EB intermediates with oxygen. Therefore, the formation of compaction products (CP) in direct EB dehydrogenation is similar to CP preceding the formation of POC. In this regard, it can be assumed that similar forms of POC arise under the influence of CO_2 with preceding CP, formed as a result of the direct dehydrogenation of EB. To confirm this assumption, comparative studies of the conversion of EB to St in the presence of carbon dioxide were carried out both on a pure catalyst sample (after regeneration) and on a sample previously brought to a stationary level by direct EB dehydrogenation. The results of these studies are shown in Figure 3, from the data of which it is seen that the conversion of EB to St in the presence of CO_2 increases with the duration of the experiment. In the case of preliminary brought of the catalyst to a stationary level, subsequent activation of the process occurs less intensively compared to a fresh catalyst sample. In this case, it can be noted that the exit of the catalyst to the stationary mode in both studied cases coincides. As mentioned above, for the development of the process of oxidative dehydrogenation of EB is responsible POC. Their formation under the influence of carbon dioxide on the stabilized during direct dehydrogenation of EB in St sample of copper-modified aluminum chromium catalyst can be caused by the interaction of CO_2 molecules with the resulting CP with transformation of them to the POC.

Identical POC are also formed on a fresh catalyst. Moreover, as can be seen from the coincidence of the time for the catalyst to reach steady-state condition, it is supposed that the process is limited by the interaction of CO_2 with the CP formed from the interaction of EB with Lewis acid centers. An additional confirmation of the proposal made on the transformation of CP into POC in the presence of CO_2 can serve as the data presented in Figure 4.

According to this figure, the data of curve 1 of Figure 3 can be straightened by representing the time of the experiment in a se-

quence known as Fibonacci series, i.e. in the sequence in which each element is the sum of 2 previous terms, i.e. $n_3 = n_1 + n_2$, $n_4 = n_2 + n_3$... etc. Such a linear dependence of unsteady conversion, which describes the activation of oxidative dehydrogenation of EB in St, when representing the experiment time in the sequence of the Fibonacci series, can mean the occurrence of two successive processes: the formation of CP, which is primary and its transition to POC as a result of interaction with CO_2 .

Thus, it can suggest the scheme for the participation of CO_2 in the oxidative dehydrogenation of EB in St:

where $\square$ – carbon defects contained in PC; $[\text{O} \dots \text{CO} - \square] [\text{O} \dots \text{CO} \dots \square]$ show the interaction of CO_2 with carbon centers (defects) containing CP, and its dissociation into an oxygen atom and CO.

Thus, CO_2 is involved in the selective oxidation of hydrogen generated during the dehydrogenation of EB. Due to this, the conversion of EB and the yield of St exceed the equilibrium

yield of St, which occurs during the direct dehydrogenation of EB. The decrease in the activity of the oxidative dehydrogenation catalyst when using CO_2 :air mixtures <3:2 is apparently due to the interaction of the $\square$ centers with oxygen and the formation of new centers according to the scheme:

An increase in oxygen concentration leads to the activation of these centers

and the course of oxidative dehydrogenation of EB in St according to the mechanism described in [31].

The effect of the copper content in aluminium-chromium contacts on the oxidative dehydrogenation of ethylbenzene to styrene was also studied. Testing of copper-modified aluminium-chromium samples in the oxidative dehydrogenation of EB in St was carried out with an oxidizing mixture of CO_2 : air = 85:15, i.e. enriched with carbon dioxide. The results of these tests are given in Table 2.

Fig. 3. The dependence of the oxidative dehydrogenation of ethylbenzene to styrene in the presence of CO_2 on the duration of the experiment: catalyst 1.5%Cu/ $\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ + 15% K_2CO_3 ; $T = 600^\circ\text{C}$, $\text{WSHV} = 2 \text{ h}^{-1}$: 1 – fresh catalyst, 2 – catalyst stabilized by direct dehydrogenation of ethylbenzene.

Fig. 4. The dependence of the oxidative dehydrogenation of ethylbenzene to styrene on the duration of the experiment the change of which is presented in the form of a Fibonacci sequence ($n_3 = n_1 + n_2$; $n_4 = n_2 + n_3$, ...): 1 – fresh catalyst, 2 – catalyst stabilized by direct dehydrogenation of ethylbenzene.

Table 2. The effect of the copper content in aluminium-chromium contacts on the oxidative dehydrogenation of ethylbenzene to styrene: $T = 600^{\circ}\text{C}$; WSHV = 2 h^{-1} ; CO_2 : air = 85:15 (vol.); $\tau = 2\text{ h}$

Content of Cu, mass. %	Specific surface area, m^2/g	Pore volume, cm^3/g	Conversion of EB, %	Selectivity for St, %	The yield of carbon by-products, mass. %			
					CH_4	C_2	C_6H_6	C_7H_8
0.5	65	0.21	33	89	0.14	0.5	1.9	2.4
1.5	67	0.23	35	91	0.15	0.5	2.0	2.4
2.5	69	0.24	37	91	0.15	0.5	1.9	2.5
3.5	71	0.27	40	86	0.21	2.7	7.6	2.5
5.0	70	0.25	39	82	0.20	2.6	8.0	2.6

From the data obtained it follows that with an increase in the copper concentration from 0.5 to 3.5%, a steady increase in the activity of the catalyst from 33 to 40% occurs. As for the selectivity of the formation of St, only on a sample with a content of 0.5% copper a slight increase in selectivity from 89 to 91% is observed. With an increase in the copper concentration to 2.5 mass%, this parameter does not change, but a further increase in the copper content leads to a noticeable decrease in the selectivity of oxidative dehydrogenation of EB in St.

The composition of hydrocarbon products formed during oxidative dehydrogenation of EB in St, are given in table. 2 as an example, shows that with small changes in the activity of the catalyst with an increase in the amount of Cu from 2.5 to 5.0%, significant changes are observed in the yields of benzene and C_2 hydrocarbons. A four- and five-fold increase in the yields of these products at almost constant degrees of EB conversion indicates that, with an increase in the copper content in the contacts, the contribution to the process reaction of hydrogenolysis of the alkyl group increases. Therefore, the optimal copper content in the aluminium-chromium contacts of oxidative dehydrogenation of EB in St should be limited to 1–2.5 mass. %.

Conclusion

Copper modified aluminum chromium catalysts, similar in composition to the hydrocarbon dehydrogenation catalysts, have high catalytic activities in the oxidative dehydrogenation of ethylbenzene to styrene in the presence of O_2 and CO_2 . The process of producing styrene from ethylbenzene on these catalysts is characterized by a high intensity (2 h^{-1}), which

is 2 to 3 times higher than the intensity of direct dehydrogenation (0.5 h^{-1}).

Aluminium-chromium catalysts modified with 1.5 mass. % Cu and promoted with 15 mass. % K_2CO_3 in the presence of carbon dioxide increase the conversion of ethylbenzene and the selectivity of styrene formation by 14 and 10%, respectively, as a result of the conversion of compaction products into oxidative compaction products. The presence of oxygen in the CO_2 :air oxidizing mixture blocks the participation of carbon dioxide in the selective oxidation of hydrogen released during the dehydrogenation of ethylbenzene.

References

1. Lebedev N.N. Khimiya i tekhnologiya osnovnogo organicheskogo sinteza. M.: Khimiya, 1988. 459 s.
2. Nederlof C., Zarubina V., Ignacio V.M.C., Erik H.J.H., Talebi H., Kapteijn F., Makkee M. Application of staged O_2 feeding in the oxidative dehydrogenation of ethylbenzene to styrene over Al_2O_3 and $\text{P}_2\text{O}_5/\text{SiO}_2$ catalysts. Applied Catalysis A: General. 2014. V. 476. P. 204–214. <https://doi.org/10.1016/j.apcata.2014.03.002>
3. Wei Liu, Chao Wang, Dangsheng Su, Wei Qi Oxidative dehydrogenation of ethylbenzene on nanocarbon: Kinetics and reaction mechanism. J. Catal. 2018. V. 368. P. 1–7. doi: 10.1016/j.jcat.2018.09.023
4. Salem C., Sadia M., Ouarda B., Smain H. Oxidative Dehydrogenation (ODH) of Ethylbenzene with CO_2 and N_2O over Heteropolycompounds. J. Chem. Sci. 2018. V. 130. Article 40. <https://doi.org/10.1007/s12039-018-1447-y>.
5. Antonio J.R.C., Joao M.S., Jouse M.F., Alcinea C.O., Adriana C., Adwin R.C.M. Oxidative dehydrogenation of ethylbenzene with CO_2 for styrene production over porous iron-based catalysts. Fuel. 2013. V. 108. P. 740–748.
6. Venkata R.B.G., Siva S.E., Suresh M., Ramudu P., Said, P., David R.B., Seetha R.R.K. The advantage of ceria loading over $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst for vapor phase oxidative dehydrogenation of ethylbenzene

- to styrene using CO₂ as a soft oxidant. *Appl. Petrochem. Res.* 2016. V. 6. P. 427–437.
7. Ramudu P., Anand N., Mohan V., Murali D.G., Prasad S.S.P., David R.B., Kamaraju S.R.R. Studies on ethylbenzene dehydrogenation with CO₂ as soft oxidant over Co₃O₄/COK-12 catalysts. *J. Chem. Sci.* 2015. V. 127. P. 701–709.
 8. Matsui J., Sodesawa T., Nozaki F. Influence of carbon dioxide addition upon decay of activity of a potassium-promoted iron oxide catalyst for dehydrogenation of ethylbenzene. *Appl. Catal.* 1991. V. 67. P. 179–188.
 9. Piotr M., Piort P., Jan O. Preparation and characterization of SBA-1-supported chromium oxide catalysts for CO₂ assisted dehydrogenation of propane. *Microporous and Mesoporous Materials.* 2012. V. 161. P. 56–66.
 10. Joao F.S. de Olivera, Diogo P.V., Jose M.C.B., Adriana P.F. Effect of CO₂ in the oxidative dehydrogenation reaction of propane over Cr/ZrO₂ catalysts. *Appl. Catal. A: Gen.* 2018. V. 558. P. 55–66.
 11. Atanga M.A., Rezael F., Jawad A., Fitch M., Rownaghi A.A. Oxidative dehydrogenation of propane to propylene with carbon dioxide. *Appl. Catal. B:Env.* 2018. V. 220. P. 429–445.
 12. Shuwei C., Zhangfeng Q., Guofu W., Mei D., Jianguo W. Promoting effect of carbon dioxide on the dehydrogenation of ethylbenzene over silica-supported vanadium catalysts. *Fuel.* 2013. V. 109. P. 43–48.
 13. Michorczyk P., Ogonowski J., Niemczyk M. Investigation of catalytic activity of CrSBA-1 materials obtained by direct method in the dehydrogenation of propane with CO₂. *Appl. Catal. A. Cen.* 2010. V. 374. P. 142–149.
 14. Mimura N., Saito M. Dehydrogenation of ethylbenzene to styrene over Fe₂O₃/Al₂O₃ catalysts in the presence of carbon dioxide. *Catal. Today.* 2000. V. 55. P. 173–178.
 15. Ventaka R.M., Kamaraju S.R.R. Advantage of Co Embedded γ -Al₂O₃ Catalysts Over MgO and SiO₂ Solid Oxides in the Selective Production of Styrene Monomer. *Catal. Lett.* 2019. V. 149. P. 3238–3252.
 16. Park M.S., Vislovsky V.P., Chang J.S., Shul Y.G., Yoo J.S., Park S.E. Catalytic dehydrogenation of ethylbenzene with carbon dioxide: promotional effect of antimony in supported vanadium–antimony oxide catalyst. *Catal. Today.* 2003. V. 87. P. 205–212.
 17. Hong D.Y., Vislovskiy V.P., Park S.E., Park M.S., Jin S.Y., Jong S.C. Dehydrogenation of Ethylbenzene with Carbon Dioxide as Soft Oxidant over Supported Vanadium-Antimony Oxide Catalyst. *Bull. Korean Chem. Soc.* 2005. V. 26. P. 1743–1748. <https://doi.org/10.5012/bkcs.2005.26.11.1743>.
 18. Cavani F., Trifiro F. Alternative processes for the production of styrene. *Appl. Catal. A. Gen.* 1995. V. 133. P. 219–239. [https://doi.org/10.1016/0926-860X\(95\)00218-9](https://doi.org/10.1016/0926-860X(95)00218-9)
 19. Nanzhe J., Abhishek B., Park S.E. Ethylbenzene to styrene over ZrO₂-based mixed metal oxide catalysts with CO₂ as soft oxidant. *Chinese Journal of Catalysis.* 2016. V. 37. P. 3–15. [https://doi.org/10.1016/S1872-2067\(15\)60901-9](https://doi.org/10.1016/S1872-2067(15)60901-9)
 20. Itika K., Venkata R.B.G., Jayesh T.B., Kamaraju S.R.R., Bhari M.M. Development of stable MoO₃/TiO₂–Al₂O₃ catalyst for oxidative dehydrogenation of ethylbenzene to styrene using CO₂ as soft oxidant. *Journ. of CO₂ utilization.* 2017. V. 18. P. 309–317.
 21. Tehua W., Siying C., Tongtong W., Huiyi L., Min J. The physicochemical properties and catalytic performance of carbon-covered alumina for oxidative dehydrogenation of ethylbenzene with CO₂. *Applied Surface Science.* 2018. V. 427. P. 1011–18. <https://doi.org/10.1016/j.apsusc.2017.08.139>
 22. Collett C.H., Gregor M.J. Things go better with coke: the beneficial role of carbonaceous deposits in heterogeneous catalysis. *Catalysis Science and Technology.* 2016. V. 6. P. 363–378.
 23. Shiju N.R., Anilkumar M., Mirajkar S.P. Oxidative dehydrogenation of ethylbenzene over vanadia-alumina catalysts in the presence of nitrous oxide: structure-activity relationship. *J. Catal.* 2005. V. 230. P. 484–492. <https://doi.org/10.1016/j.jcat.2005.01.010>
 24. Zhyznnevskiy V.M., Tsybukh R.D., Gumenetskiy V.V., Kochubeiy V.V. Physico-chemical and catalytic properties of Fe₂BiMo₂O_x catalyst ultrasound treated and promoted with Al₂O₃ in the oxidative dehydrogenation of ethylbenzene to styrene. *App. Catal. A. Gen.* 2002. V. 238. P. 18–28.
 25. Mamedova M.T. Dehydrogenation of ethylbenzene in styrene on MgO,ZrO₂/Al₂O₃ catalyst. *Pros. Petr. & Oil Ref.* 2019. V. 20. No 4. P. 347–355.
 26. Mamedova M.T. Okislitelnoe degidrirovanie etilbenzola v stirol na otrabotannom aliumokhromovom katalizatore. *Zhurn. prikladnoi himii.* 2020. V. 93. T. 4. C. 483–489.
 27. Abasov S.I., Asadov N.S., Zarbaliev R.R., Nasirova F.M., Tagiev D.B. Degidrirovanie etilbenzola v prisutstvii kisloroda na aliumomedny`kh katalizatorakh. *Protcessy` Neftehimii i Neftepererabotki.* 2010. № 4. S. 329–333.
 28. Kry`lov O.V. Geterogenny`i` kataliz. M.: IKTC Akademkniga. 2004. S. 590– 91.
 29. Alhazov T.G., Margolis L.Ia. Vy`sokoselektivny`e katalizatory okisleniia uglevodorodov. M.: Himiia. 1988. 186 s.
 30. Abasov, Asadov N.S., Zarbaliev Z.Z., Nasirova F.M., Tagiev D.B. Degidrirovanie e`tilbenzola v prisutstvii kisloroda na aliumomedny`kh katali-

- zatorakh. Protcessy Neftehimii i Neftepererabotki. 2010. № 4. S.329–333.
31. Krylov O.V. Geterogenyi kataliz. M.: IKTC Akademkniga. 2004. S. 590–591.
32. Alhazov T.G., Margolis L.Ia. Vysokoselektivnye katalizatory okisleniya uglevodorodov. M.: Himia. 1988. 186 s.

ETİLBENZOLUN ALÜMOXROM KATALİZATORLARININ İŞTİRAKI İLƏ OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏSİNƏ KARBON DİOKSİDİN TƏSİRİ

M.T.Məmmədova

Əmələ gələn hidrogenin selektiv oksidləşdirilməsi yolu ilə etilbenzoldan stiroulun daha səmərəli alınma prosesinin yaradılması məqsədilə mislə modifikasiya olunmuş alümoxtrom katalizatorları hazırlanmış və onların aktivliyi O_2 (hava), CO_2 və CO_2 : hava qarışığının iştirakıbdə öyrənilmişdir. Məlum olmuşdur ki, sintez olunmuş alümoxtrom katalizatorları üzərində etilbenzoldan stiroulun alınması prosesi yüksək intensivliklə gedir. Mislə modifikasiya olunmuş və 15 kütl.% K_2CO_3 ilə promotorlaşdırılmış alümoxtrom katalizatorları CO_2 -nin iştirakında üzərlərində əmələ gələn sıxlaşma məhsullarının oksidləşdirici sıxlaşma məhsullarına çevrilməsi hesabına etilbenzolun konversiyasını 14, stirola görə selektivliyi isə 10% yüksəldirlər. CO_2 :hava oksidləşdirici qarışığındakı oksigen etilbenzolun birbaşa dehidrogenləşməsindən əmələ gələn hidrogenin selektiv oksidləşdirilməsində CO_2 -yə mane olur. Məlum olmuşdur ki, tərkibində 1.5–2.5% modifikator (Cu) olan alümoxtrom katalizatoru etilbenzolun stirola oksidləşdirici dehidrogenləşməsində daha yüksək selektivliyə malikdir.

Açar sözlər: *Etilbenzol, stirol, oksidləşdirici dehidrogenləşmə, model alümoxtrom katalizatorları, mislə modifikasiya, CO_2 :hava oksidləşdirici qarışığı, CO_2 , sıxlaşma məhsulları, oksidləşmiş sıxlaşma məhsulları.*

ВЛИЯНИЕ ДИОКСИДА УГЛЕРОДА НА ОКИСЛИТЕЛЬНОЕ ДЕГИДРИРОВАНИЕ ЭТИЛБЕНЗОЛА В ПРИСУТСТВИИ АЛЮМОХРОМОВЫХ КАТАЛИЗАТОРОВ

М.Т.Мамедова

С целью создания более эффективного процесса получения стирола из этилбензола путем селективного окисления образующегося водорода приготовлены модельные алюмохромовые катализаторы с различным содержанием модификатора (Cu), а в качестве окисланта использованы O_2 , CO_2 и смесь CO_2 :воздух. Установлено, что процесс получения стирола из этилбензола на алюмохромовых катализаторах характеризуется высокой интенсивностью. Алюмохромовые катализаторы, модифицированные Cu и промотированные 15 мас.% K_2CO_3 , в присутствии диоксида углерода повышают конверсию этилбензола на 14%, а селективность образования стирола на 10% в результате перехода продуктов уплотнения в продукты окислительного уплотнения. Наличие кислорода, в окислительной смеси CO_2 : воздух, блокирует участие диоксида углерода в селективном окислении водорода, выделяющегося при дегидрировании этилбензола. Установлено, что наиболее селективные в окислительном дегидрировании этилбензола в стирол алюмохромовые катализаторы, содержат 1.5–2.5 мас. % модифицирующего компонента (Cu).

Ключевые слова: *этилбензол, стирол, окислительное дегидрирование, модельные алюмохромные катализаторы, модификация медью, окислительная смесь CO_2 :воздух, CO_2 , продукты уплотнения, продукты окислительного уплотнения.*