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CATALYTIC PROPERTIES OF MODIFIED IRON-CHROMIUM-POTASSIUM SYSTEMS IN THE THERMOCATALYTIC DEHYDROGENATION OF ETHYLBENZENE

Abstract. The comparison of the efficiency of iron oxide catalytic systems modified with additions of cerium and zirconium oxides in the dehydrogenation of ethylbenzene to styrene was considered. According to the yield of the desired product (styrene), cerium- and zirconium-containing contacts exceed the unmodified Fe-K-Cr-O catalyst. Styrene is obtained about the yield of 79 % at 630 °C, ethylbenzene load of 150 g per liter of catalyst per hour and a molar ratio of water:ethylbenzene = 17,4.

Key words: dehydrogenation, ethylbenzene, styrene, catalysts.

Introduction. Styrene is one of the most important petrochemical product, which use as raw material for polymer production (polystyrene, synthetic rubber) and copolymers (impact-resistant polystyrene based on acrylonitrile and butadiene). The styrene production is a large-tonnage, the volume of styrene production is over 30 million tons per year [1]. There has been a recovery in styrene production in Russia over the last three years. In 2017, Russia produced 69 1748 tons of styrene [2], which is 1.3% more than the previous year.

About 90 % of the world styrene production (ST) is realized by the dehydrogenation of ethylbenzene (EB). The process is carried out at the presence of an iron oxide catalyst in the gas phase at 580-630 °C. The producers of iron oxide catalysts in Russia are OJSC "Kauchuk" (Sterlitamak), OJSC "SRI Yarsintez" (Yaroslavl) and OJSC "Nizhnekamskneftekhim", and foreing overseas – companies such as Shell, Sud Chemie, BASF and others [3,4]. The main component of all catalysts of the listed companies is iron oxide, promoted by compounds of alkali, alkaline-earth, transition and rare-earth metals. The efficiency of the catalyst depends on the content and nature of the catalytically active component, the presence of modifying additives and the technology for manufacturing the catalyst.

Additives to iron oxide take a special role in the formation of the catalysts properties. For example, in its work D.V. Kachalov [5] showed that the compounds of cerium and molybdenum significantly increase the electron-exchange rate, etween of Fe^{2+}/Fe^{3+}, thereby contributing to the oxidation-reduction mechanism of catalysis. When studying the influence of cerium oxide on the formation of the active phase, it was noted by Dementieva E.V. that cerium oxide interferes with the formation of potassium polyferrites, and in the topochemical reaction of hematite with potassium carbonate, potassium monoferrites are mainly formed. The author assumes that the introduction of cerium compounds leads to the dispersion of the polyferritic phase and the secondary particles (agglomerates) of the catalyst, accompanied by an increase of the specific surface [6]. The authors of the work [7] showed that the modification of aluminum oxide with additives of ZrO_2 and/or CeO_2 resulted in a significant increase in the activity of Cr-containing catalysts.

A.A. Emekeyev with contributors [8] investigated the effect of iron oxide compounds, as well as alkali metals, rare-earth elements and transition metals with several common oxidation states on the catalytic activity in the ethylbenzene dehydrogenation reaction to styrene. The introduction of cerium or molybdenum compounds into the catalyst composition leads to an increase in the selectivity of the process up to 88.0-90.7 % and a relatively small increase in the conversion of ethylbenzene with the iron- cerium-oxide (Fe-Ce-O) system.

Analysis of literature data showed that, despite the fact that iron oxide contacts have long been used in industry, research continues on the nature of their catalytic activity and the effect of promoters on activity.

This article is devoted the development of modified iron oxide catalysts for dehydrogenation of ethylbenzene in order to improve their catalytic properties.

EXPERIMENTAL PART

Experimental researches of catalytic dehydrogenation ethylbenzene (EB) were carried out on a flow reactor with a fixed-bed catalyst at the presence of water vapor.

In our work we used freshly distilled ethylbenzene (boiling temperature 136 °C), obtained at the Aktau Plastics Plant by catalytic alkylation of benzene with ethylene. Experiments of dehydrogenation ethylbenzene were carried out on the flow reactor (300 mm in length and an internal diameter of 8 mm). The catalysts were prepared by mixing the calculated amounts of iron oxides, chromium (III) and potassium carbonate, which had been pre-ground thoroughly in a mortar. The resulting charge was compressed into tablets, which were dried for 2 hours at 150 °C and calcined at 800 °C for 2 hours. The calcined tablets were ground to particles of 1-3 mm in size. 10 ml of catalyst was charged into the reactor.

To test the synthesized catalysts, the operating mode of the K-24 catalyst used in industry was adopted as a basis.

Turning on the nitrogen supply ($20 L \cdot h^{-1}$), heating furnace and evaporator, at 350 °C, water is supplied to the evaporator at rate of $174\ g \cdot h^{-1}$. The nitrogen supply is stopped. The reactor is heated to 650 °C and the catalyst is maintained in a stream of steam for 2 hours. At the end of the exposure, the temperature is lowered to 550 °C and the ethylbenzene supply starts at a rate of $10\text{-}14\ g \cdot h^{-1}$. After 30 minutes the supply is increased to $24\text{-}30\ g \cdot h^{-1}$, the temperature - up to 570 °C. After another 60 minutes the supply is increased to $40\ g \cdot h^{-1}$ and the temperature - up to 600 °C. The catalyst test is started after 120 minutes.

The reaction products were captured in scrubbers of airlift type irrigated with acetone. Gas chromatographic analysis of the reaction products were carried out by chromatograph "Color-106" with a flame ionization detector; a glass column 1000 × 4 mm in size, filled with a fixed phase of 25% PEGA + 2% H_3PO_4 on an INZ-600 carrier. Gas carrier- Argon, and column temperature is 90 ^oC.

RESULTS AND DISCUSSION

The process of thermocatalytic dehydrogenation of ethylbenzene to styrene is widely considered in the literature, and a lot of catalysts are described. One of the main component is Fe_2O_3, which initial presence is 55-85 %. However, in many cases, the conversion of the initial product is only 50-75 %. According to this, the search for the new efficient catalytic systems continues.

Catalytic activity and selectivity of dehydrogenation catalysts are due to their chemical composition, crystal lattice structure and surface size.

The active components of iron-oxide systems in the dehydrogenation reaction are potassium ferrites, which formation occurs during the preparation and activation of the catalyst.

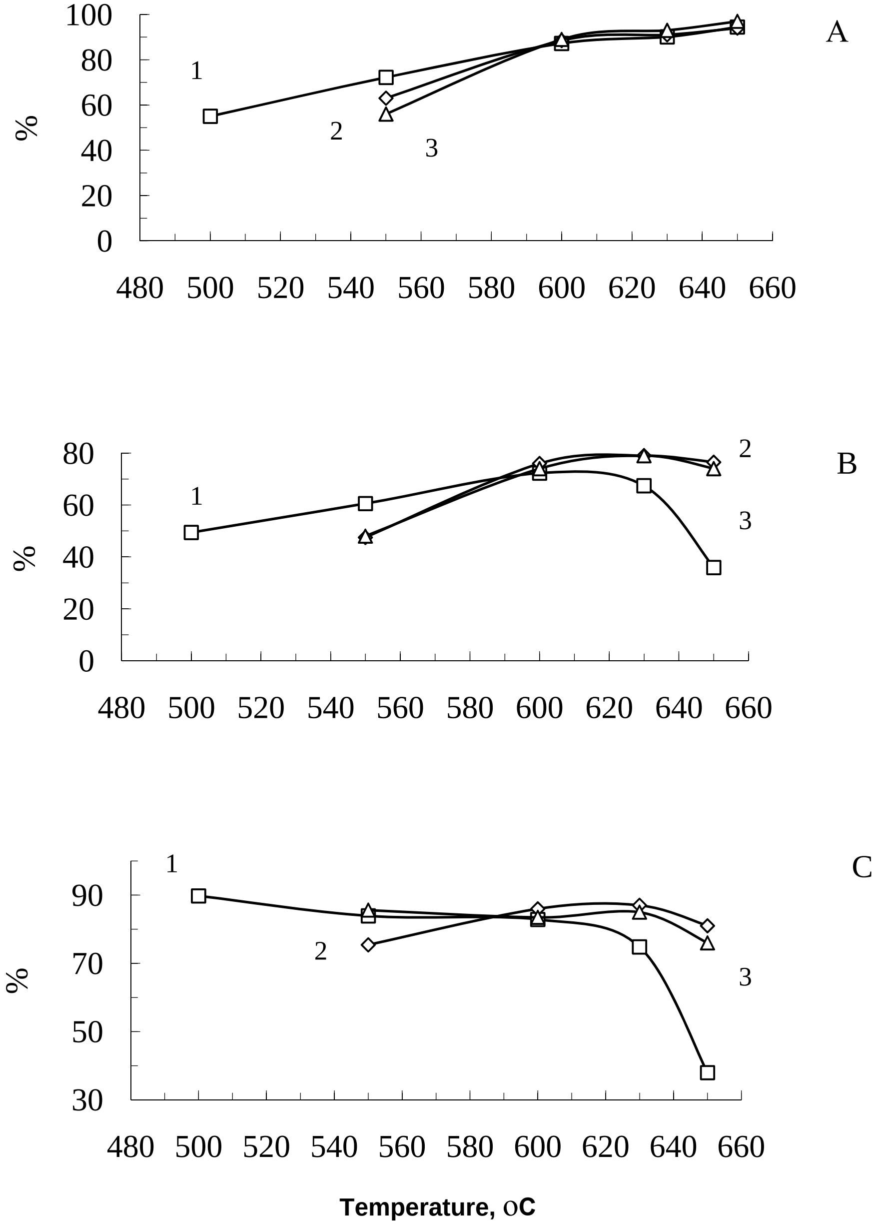
It is possible to change the catalyst properties at various stages of preparation in order to create highly effective connections.

In chemical technology the technological conditions of the process are of great importance, therefore, the dependence of the EB conversion, the styrene (ST) yield and the selectivity of its formation on the dehydrogenation temperature, the supply rate of EB and the ratio of dilution on the dehydrogenation process have been studied.

There are side processes in the process of dehydrogenation of ethylbenzene along with the main reaction, such as: coking, isomerization and cracking. Cracking and isomerization reduce the selectivity of the process, and coking has an effect on catalyst deactivation. If we want the catalyst work for a longer-term period, it is necessary to carry out periodic oxidative regeneration, as a result of which coke is burnt off from the catalyst surface.

Initially, a triple Fe-Cr-K-oxide system of 85 % Fe_2O_3-10 % K_2O-5 % Cr_2O_3, which is the basis of industrial catalysts, was tested in the thermocatalytic dehydrogenation of ethylbenzene. The conversion of ethylbenzene on this sample at 600 °C was 87.2 %, at the maximum yield of styrene 72 %.

Further, the catalytic activity of iron-chromium-potassium catalysts modified with additives of zirconium and aluminum oxides were investigated. When testing catalyst samples, the ethylbenzene supply rate was 153 g., water - 450 g. per 1 lt. of catalyst per an hour, which corresponded to a molar ratio of ethylbenzene: H_2O = 1:17.4. Dehydrogenation of ethylbenzene was carried out at the range temperature from 550 to 650 °C. The obtained results showed that the introduction of zirconium dioxide and aluminum oxide in the compound of iron-chromium-potassium catalyst increased its catalytic activity: an increase in the conversion of the initial product up to 94% was observed. Styrene was obtained with the highest yield (69-72 %) on the unmodified Fe-Cr-K-O catalyst prepared by the dry oxide tableting method. On the catalyst with the addition of zirconium dioxide, the yield



Influence of temperature on conversion of ethylbenzene (A), yield (B) and selectivity of styrene formation (C) on modified catalysts.

The supply rate of ethylbenzene - 1.53 g, water - 4.5 g., nitrogen 12.4 L. per hour. The molar ratio of ethylbenzene:H_2O = 1: 17.4. Catalysts:1- 85 % Fe_2O_3 -10 % K_2O - 5 % Cr_2O_3; 2 - 45,87 % Fe_2O_3 - 20,29 % K_2O - 5,46 % Cr_2O_3 - 6,53 % V_2O_5 -12,36 % CeO_2; 3 – 47,54 % Fe_2O_3 - 21,03 % K_2O - 5,66 % Cr_2O_3 - 6,77 % V_2O_5 - 9,17 % ZrO_2.

of styrene at 600 °C reached 69 %, andat the somtime it was 42-46 % on the iron-chromium-potassium catalyst modified with aluminum oxide.

Next step is that catalyst samples containing vanadium pentoxide were synthesized by the method of mixing dry components. The number of main components varied within the limits: Fe_2O_3 - 45-85 %, K_2O - 10-21 %, Cr_2O_3 - 5-6 %, V_2O_5 - 6.5-6.8 %. Additionally, cerium and zirconium oxides were introduced in these catalysts. Influence of the temperature, contacting time and amount of nitrogen and water vapor supplied to the catalysis zone on the yield of the main reaction products (styrene, toluene, benzene, unreacted ethylbenzene) were studied.

As part of experimental studies it was found that the dehydrogenation of EB on catalysts modified with cerium and zirconium oxides in the presence of water, the general regularities of the influence of dehydrogenation conditions on the process parameters are preserved, while achieving a higher yield of ST at the temperature of the dehydrogenation process - 630 °C. The figure shows the dependence of the conversion of the initial ethylbenzene, the yield and the selectivity of the desired product formation versus of temperature on Fe-Cr-K-V-Ce-O and Fe-Cr-K-V-Zr-O contact. The maximum conversion of ethylbenzene has been achieved on a Fe-Cr-K-V-Zr-O catalyst and was 97 % at 650 °C. As it is seen from the figure that on both tested catalysts styrene was obtained about yield of 79 % at 630 °C, ethylbenzene load of 150 g. per liter of catalyst per hour and a molar ratio of water:ethylbenzene = 17.4.

Conclusion. The obtained results indicate that these catalysts are sufficiently effective for thermocatalytic dehydrogenation of ethylbenzene to styrene. Apparently, the additions of zirconium and cerium oxides influence the formation of potassium ferrites, determining the activity of the tested catalytic systems in the ethylbenzene dehydrogenation reaction. Adding vanadium and/or cerium, zirconium oxides to the three-component Fe-K-Cr-O catalyst resulted in an increase in the yield of styrene from 72 to 79 %. The selectivity of styrene formation on the iron-oxide catalyst modified by ZrO_2 in the temperature range of 550-600 °C was 85.6-83.5 %, and on Fe-Cr-K-V-Ce-O connection - 86-87 % (600-630 °C).

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Резюме

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МОДИФИЦИРЛЕНГЕН ТЕМІР-ХРОМ КАТАЛИЗАТОРЛАРЫНДА ЭТИЛБЕНЗОЛДЫҢ ТЕРМОКАТАЛИТИКАЛЫҚ ДЕГИДРЛЕНУІН ЗЕРТТЕУ

Этилбензолды церий және цирконий оксидтерімен модифицирленген темір-хром оксидті катализаторларында дегидрлеуді зерттеу.

Түйін сөздер: дегидрирлеу, этилбензол, стирол, катализаторлар

Резюме

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КАТАЛИТИЧЕСКИЕ СВОЙСТВА МОДИФИЦИРОВАННЫХ ЖЕЛЕЗОХРОМКАЛИЕВЫХ СИСТЕМ В ТЕРМОКАТАЛИТИЧЕСКОМ ДЕГИДРИРОВАНИИ ЭТИЛБЕНЗОЛА

Обсуждено влияние оксидов церия и циркония на каталитические свойства железооксидного контакта в термокаталитическом дегидрировании этилбензола.

Ключевые слова: дегидрирование, этилбензол, стирол, катализаторы.