Prodicing Mesitylene by Dehydrotreatment of C_9-aromatics Distilled from Coal Pyrolysis Products

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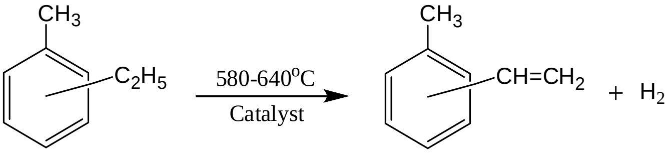
Abstract – **The paper describes the results of studies on improving nickelia-vanadia-based catalyst for ethyltoluenes dehydrogenation and the features of the process for mesitylene production on its base. This process (dehydrotreatment of C_9-aromatics) includes catalytic removal of ethyltoluene impurities from C_9 fractions of coal pyrolysis products, followed by isolation of the target product by two-step fractionation of the dehydrogenate obtained. The optimal composition of the catalyst for this process has been determined, and operating conditions for catalytic treatment of C_9 fractions in its presence have been chosen. The advantage of using coal-derived C_9-aromatics as feedstocks for the proposed dehydrotreatment process, in comparison with analogous petroleum-derived C_9 fractions, is emphasized. The technological scheme of the given process is presented, and its performance characteristics are compared to corresponding parameters of some alternative methods of mesitylene production. Relative simplicity, feasibility, good quality of commercial mesitylene produced (of ≥ 98.8% purity), combined with high efficiency of its recovery from C_9 fractions of hydrocarbons (up to 82.5% from its resources in the feedstock), are the essential features of the technology proposed.**

Keywords – mesitylene; C_9 fractions of coal pyrolysis products; $Na_2O\text{-}NiO\text{-}V_2O_5/\gamma\text{-}Al_2O_3$ catalyst; ethyltoluenes; dehydrotreatment; activity; selectivity

I. INTRODUCTION

One of the main directions for deep processing of solid fuels is production of valuable chemical compounds from the products of their thermal and catalytic transformations [1]. These valuable chemical materials and reagents can be used as the feedstock for various processes of organic synthesis. In particular, mesitylene (1,3,5-trimethylbenzene) is considered to have a great interest among the chemicals of such kind since it is employed in the processes of obtaining mesidine, trimesic acid, mesitol, triisocyanates and polyurethanes on their base, as well as for synthesis of some pharmaceuticals. Quite substantial resources of mesitylene (7-17 wt.%) are contained in so called C_9 fractions of aromatic hydrocarbons distilled from products of coal pyrolysis and residues of reforming gasoline [2, 3]. However, very pure mesitylene (of ≥ 98 wt.% purity) is required for modern technological processes, while during simple rectification of mesitylene from C_9 hydrocarbons its yield is too low because of a small difference between boiling points of mesitylene and ethyltoluene isomers that form azeotropic mixtures with mesitylene. Therefore, yield of mesitylene of even ~ 78% purity does not exceed 50÷60% in this case [2]. And these values tend to worsen with increasing concentration of ethyltoluens in C_9 fractions.

There are various approaches for solving the problem of mesitylene separation from ethyltoluenes (in particular, chemical, physical-chemical and catalytic methods of ethyltoluenes removal) [4]. But the most of them is characterized by a number of serious shortcomings hindering to realize the given technologies in industrial practice (insufficiently high quality of mesitylene produced, usage of unstable and toxic reagents, multi-stage process of refining and complexity of apparatus design, very severe requirements on mesitylene content in the initial feedstock, high losses of the target product, etc.). In our opinion, one of the simplest ways to recover mesitylene from technical C_9 fractions of aromatic hydrocarbons is a preliminary removal of ethyltoluenes (by converting them into vinyltoluenes easily separable from mesitylene by rectification) from these fractions during the catalytic treatment of mesitylene-containing feedstocks in the presence of dehydrogenation catalysts [5-7]:



This allows one to significantly reduce the content of ethyltoluene impurities without marked losses of the target product since side reactions (cracking, dealkylation and isomerization) contribution into the distribution of conversion products of alkylbenzenes in the presence of dehydrogenation catalysts is negligible [5, 6]. Such a process (so called dehydrotreatment or dehydrorefining) proceeds in the presence of dehydrogenation catalysts at the temperatures of 580-640°C, under atmospheric pressure, at liquid hour space velocities ($LHSV_{C9}$) of 0.1÷0.8 h^{-1} and at feed (C_9 hydrocarbons)/water steam mass ratios of ~ 1/1÷5. After this catalytic treatment finished, vinyltoluenes formed are removed from water-separated dehydrogenate by either simple rectification or chemically [6]. Well known chromia-alumina

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catalysts were not suitable for this process, as they significantly intensified undesired reactions of C_9-aromatics cracking and dealkylation, and it reduced selectivity to dehydrogenation products [5]. Also, commercial iron-chromium-potassium (Fe-Cr-K) catalyst used in the industrial process of ethylbenzene dehydrogenation to styrene was insufficiently effective in the given case (vinyltoluenes yields in its presence did not exceed 32÷37% per one pass at selectivity to vinyltoluenes of ~ 45÷57%). From dehydrogenate produced in the presence of Fe-Cr-K catalyst, mesitylene of only 84.89% purity could be obtained, which contained up to 2.08% ethyltoluenes [5]. Besides that, high-purity C_9-fractions and frequent regenerations were required for stable work of Fe-Cr-K catalyst during dehydrotreatment of mesitylene-containing feedstocks. Relatively acceptable technical characteristics for the process considered (conversion of ethyltoluenes to vinyltoluenes of ~ 31% and selectivity to vinyltoluenes of ~ 90%) were only achieved by using Na_2O-Cr_2O_3-MoO_3/γ-Al_2O_3 catalyst (its chemical composition, wt.%: 9÷15 MoO_3, 5÷25 Cr_2O_3, 0.1÷5.0 Na_2O, the rest is γ-Al_2O_3) with multifold recycle of the reaction products [6, 7]. This allowed to obtain mesitylene of 98.73% purity with recovery efficiency of 78.2% from mesitylene resourses in the initial feedstock [6].

It is obvious that in case of using more efficient dehydrogenation catalysts providing deeper conversion of ethyltoluenes, the yield and purity of mesitylene produced can be improved. In this connection, it should be noted that supported vanadium oxide-based systems are rather active catalysts for both non-oxidative and oxidative dehydrogenations of hydrocarbons [8-12]. Moreover, dehydrogenation activity and work stability of vanadia-based catalysts are sometimes comparable or even superior to those of chromia- and Pt-based ones widely used in industrial dehydrogenation processes [11, 12]. Therefore, there was a certain interest to examine the activity of vanadia-based systems in dehydrotreatment of C_9-aromatics. And indeed, recently catalytic compositions on the base of γ-alumina supported vanadium (V), nickel (II) and sodium oxides have been successfully employed for removal of ethyltoluenes from mesitylene-containing fractions [13]. Moreover, these compositions exhibited higher activity and selectivity in dehydrogenation of ethyl-substituted benzene derivatives, than the above mentioned Na_2O-Cr_2O_3-MoO_3/γ-Al_2O_3 catalyst [13].

This paper describes the results of studies on optimization of the chemical composition for Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst, data on the choice of its exploitation conditions and recovery efficiency of commercial mesitylene from C_9-aromatics dehydrotreated in its presence.

II. MATERIALS AND METHODS

For the choice of the optimal composition of Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst, several series of γ-alumina supported catalysts having various amounts of vanadium (V) and nickel (II) oxides have been prepared: 1) 2 wt.% Na_2O - (0÷20) wt.% V_2O_5/γ-Al_2O_3; 2) 2 wt.% Na_2O - (0÷5) wt.% NiO – 10 wt.% V_2O_5/γ-Al_2O_3 and 3) (0÷3) wt.% Na_2O – 1 wt.% NiO – 10 wt.% V_2O_5/γ-Al_2O_3. These samples have been synthesized by sequential impregnation of commercial γ-Al_2O_3 (A-64, S = 200 m^2/g, average pore radius of ~ 10 nm) with aqueous solutions of NH_4VO_3, $Ni(NO_3)_2 \cdot 6H_2O$ and Na_2CO_3, followed by drying (120°C, 4 h) and calcining (600°C, 6 h) in air after each component deposition. All the samples prepared were promoted by 2 wt.% Na_2O to suppress acidic sites catalyzing undesired reactions of cracking and dealkylation of hydrocarbons, as well as processes of catalyst coking. Similarly, a series of γ-alumina supported NiO-V_2O_5 compositions with various NiO/(NiO+V_2O_5) molar ratios at constant total amount of the given components (NiO+V_2O_5 = 11 wt.%), has been synthesized; all these samples were also modified with 2 wt.% Na_2O. For comparison, a series of unsupported binary NiO-V_2O_5 samples with NiO/(NiO+V_2O_5) molar ratios from 0 to 1 has been prepared by mixing aqueous solutions of corresponding amounts of NH_4VO_3 and $Ni(NO_3)_2 \cdot 6H_2O$, followed by drying (120°C, 4 h) and calcining (600°C, 6 h) in air of evaporated precipitates. All the synthesized catalysts were characterized by X-ray diffraction (XRD) method (a HZG-4.0 instrument; Ni-filtered CuK_α-irradiation).

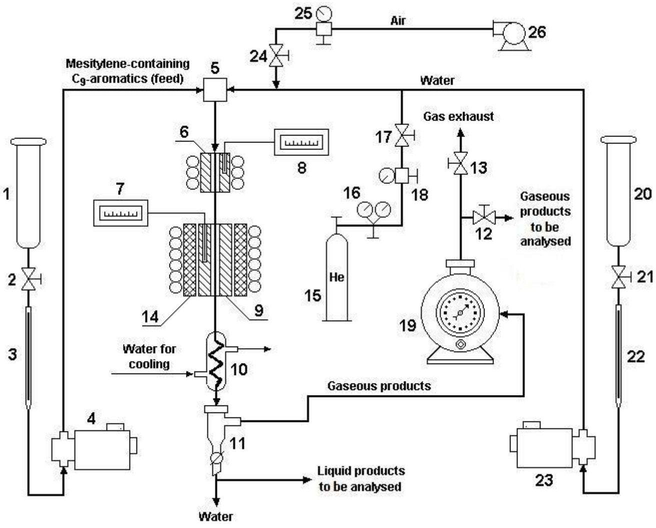

Fig. 1. Scheme of a laboratory flow catalytic setup for dehydrotretment of mesitylene-containing hydrocarbon fractions:

1 – vessel with mesitylene-containing fractions of hydrocarbons; 2,12,13,17,21,24 – valves; 3,22 – burettes; 4 – dosing pump for feeding hydrocarbons; 5 – mixer; 6 – evaporator (preheater); 7,8 – temperature regulators; 9 – reactor; 10 – cooler; 11 – separator; 14 – copper insert for diminishing temperature gradients in the catalyst layer; 15 – helium balloon; 16 – gas pressure reductor; 18,25 – gas flow regulators; 19 – gas clock; 20 – vessel with water; 23 – dosing pump for feeding water; 26 – air compressor (for catalyst regeneration)

Dehydrogenation activities of the catalysts prepared were studied using a conventional pulse microcatalytic setup of a “reactor-cromatograph” type (similar to that described in [14]) in a model reaction of ethylbenzene conversion. Chromatographic analysis conditions of the components were the following: detector – catharometer; stainless steel chromatographic column 6 m length and internal diameter of ~ 3 mm, filled with PEGA (9 wt.%) + 1,2,3-Tris(2-

cyanoethoxy)propane (1.6 wt.%)/Dinochrom-N (0.315-0.500 mm); gas-carrier (helium) flow rate ~ 60 ml/min. Catalytic properties of the samples were estimated by styrene yields and selectivities of the reaction to styrene under the following conditions: T = 620°C; P = 0.1 MPa; τ_c = 1 s; volume of ethylbenzene pulse ~ 2 mcl.

Catalytic runs on optimization of operating conditions for dehydrotreatment process were carried out using a laboratory catalytic flow setup depicted in Fig. 1. These experiments were performed in the presence of Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst (volume of catalyst charge ~ 40 cm^3) at the temperatures (T) of 600÷650°C, at liquid hour space velocities of C_9 fractions of hydrocarbons ($LHSV_{C9}$) of 0.1÷0.8 h^{-1} and at dilutions of C_9 hydrocarbons with water steam (H_2O/feed mass ratios) from 3:1 to 7:1. An ethyltoluene-enriched fraction of C_9 hydrocarbons (b.p. ~ 155-161°C; content of ethyltoluenes – 62.4 wt.%) distilled by rectification from post-xylene fraction reformate was used as the initial feedstock in these experiments. The initial feedstocks and products of their transformations were analysed chromatographically according to the techniques described in [14, 15]. The efficiency of ethyltoluenes conversion during the catalytic treatment of C_9 fractions of hydrocarbons was estimated by yields of vinyltoluenes per passed [beta] and converted [gamma] ethyltoluenes.

Three types of narrow C_9 fractions of aromatic hydrocarbons were chosen as mesitylene-containing feedstocks for the experiments on pure mesitylene production: 1) a fraction distilled from Kansk-Achinsk brown coal flash pyrolysis tar (b.p. ~ 164-165°C); 2) a fraction distilled from a coke-oven solvent (b.p. ~ 161-166°C) and 3) a fraction distilled from gasoline reforming products (b.p. ~ 161-166°C). Catalytic treatment of these fractions was carried out in the presence of 2 wt.% Na_2O - 1 wt.% NiO - 10 wt.% V_2O_5/γ-Al_2O_3 catalyst at T ~ 620÷640°C, $LHSV_{C9}$ ~ 0.3÷0.4 h^{-1} and H_2O/feed mass ratios ~ 4÷5/1.

Water-separated dehydrogenates obtained after dehydrotreatments of the given fractions were preliminarily divided into three parts (b.p. < 163°C, b.p. ~ 163-165°C and b.p. > 165°C) with a laboratory rectification column of ~ 20 theoretical plates efficiency at a reflux ratio of ~ 25. Then, using a laboratory rectification column of ~ 40 theoretical plates efficiency at a reflux ratio of ~ 30, pure mesitylene was distilled from mesitylene-enriched part (b.p. ~ 163-165°C) in the temperature range 164.6÷164.8°C. The efficiency of mesitylene recovery was estimated by the yield of mesitylene in % from its resources in the initial feedstock.

III. RESULTS AND DISCUSSIONS

Results of pulse catalytic measurements are presented in Figures 2-5. As it can be seen from Figure 2, the dehydrogenation activity of 2 wt.% Na_2O - (0÷20) wt.% V_2O_5/γ-Al_2O_3 systems at first increased with V_2O_5 contents, but at V_2O_5 loadings higher than 10 wt.%, it goes to a constant level. This concentration level of V_2O_5 (~ 10 wt.%) can apparently be considered as the optimal one for γ-alumina supported V_2O_5-based dehydrogenation catalysts.

Adding the small amounts of NiO to a 2 wt.% Na_2O -10 wt.% V_2O_5/γ-Al_2O_3 system resulted in the marked increase in styrene yield. But at already NiO loadings > 1 wt.%, the side reactions of ethylbenzene cracking and dealkylation sharply intensified, and it facilitated quick coking of the catalysts and reduction their selectivity to styrene (Fig. 3). Sodium effects are similar to those of nickel doping. At small Na_2O loadings, dehydrogenation activities and selectivities to styrene for x wt.% Na_2O – 1 wt.% NiO - 10 wt.% V_2O_5/γ-Al_2O_3 samples tended to rise with sodium content, but with increasing Na_2O concentrations higher than 2 wt.%, ethylbenzene conversion significantly decreased while styrene yield fell down to 48÷50% (Fig. 4). Maximal styrene yields (80÷81%) and selectivities to styrene (90÷95%) were observed for Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst having the following chemical composition, wt.%: V_2O_5 ~ 10; NiO ~ 1 and Na_2O ~ 2. This optimized chemical composition for the given catalyst was further used in the flow catalytic experiments.

TABLE I. PHASE COMPOSITION OF SYNTHESIZED OF UNSUPPORTED AND γ-AL_2O_3 SUPPORTED NIO-V_2O_5-BASED CATALYSTS WITH VARIOS NIO/V_2O_5 MOLAR RATIOS

NiO-V_2O_5 catalysts		**Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalysts[a]**	
Ratio[b]	**Phase composition[c]**	**Ratio[b]**	**Phase composition[c]**
0.00	V_2O_5	0.00	γ-Al_2O_3
0.10	V_2O_5	0.10	γ-Al_2O_3
0.20	V_2O_5	0.20	γ-Al_2O_3
0.30	$Ni(VO_3)_2$; V_2O_5	0.35	γ-Al_2O_3
0.50	$Ni(VO_3)_2$	0.48	γ-Al_2O_3
0.60	$Ni_2V_2O_7$; $Ni(VO_3)_2$	0.67	γ-Al_2O_3
0.75	$Ni_3(VO_4)_2$; NiO	0.81	γ-Al_2O_3
0.90	NiO	0.89	γ-Al_2O_3; traces of $NiAl_2O_4$
1.00	NiO	1.00	γ-Al_2O_3; $NiAl_2O_4$

[a] Total (NiO+V_2O_5) content = 11 wt.%; all the supported catalysts were additionally modified by 2 wt.% Na_2O.

[b] NiO/(NiO+V_2O_5) molar ratio.

[c] The phases are arranged in descending order of their most intense XRD lines.

For binary NiO-V_2O_5 compositions and Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalysts having various ratios of nickel (II) and vanadium (V) oxides, dehydrogenation activity maxima were observed at NiO/(NiO+V_2O_5) molar ratios ~ 0.15 (i.e. at the areas of relatively small nickel concentrations); further increase in NiO content drastically worsens dehydrogenating properties of NiO-V_2O_5-based systems (fig. 5). Coincidence of dehydrogenation activity maxima for unsupported and supported NiO-V_2O_5-based samples appears to be not casual; this may be due to the similar nature of active sites, which are present in both series of these catalysts and are taking part in the reaction considered.

Phase compositions of synthesized unsupported and γ-alumina supported NiO-V_2O_5-based samples with various molar ratios of nickel (II) and vanadium (V) oxides are listed in Table 1. In addition to the initial phases of NiO and V_2O_5, the phases of nickel (II) meta-, pyro- and ortho-vanadates were also identified in a binary NiO-V_2O_5 system. According to the XRD data, the supported components in Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalysts were mostly röntgenamorphous (only γ- Al_2O_3 spinel phase lines were fixed in the X-ray diffraction patterns of these catalysts) (Table 1). Similar XRD patterns were also observed for series of γ-Al_2O_3-based catalysts with various concentrations of the supported components. This points to a highly dispersed state of nickel (II) vanadium (V) oxides on the support surface. However, in the samples with the highest NiO contents [NiO/(NiO+V_2O_5) ≥ 0.89], weak XRD lines from bulk $NiAl_2O_4$ phase (*d/n* ~ 2.41 Å) have been also detected.

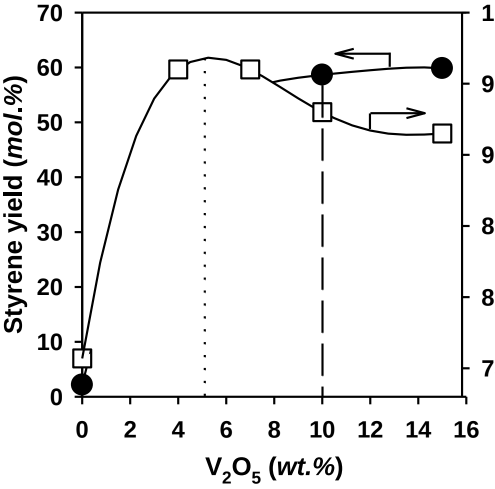

Fig. 2. Effect of V_2O_5 content on the activity and selectivity of 2 wt.% Na_2O - x wt.% V_2O_5/γ-Al_2O_3 catalysts in the reaction of ethylbenzene dehydrogenation

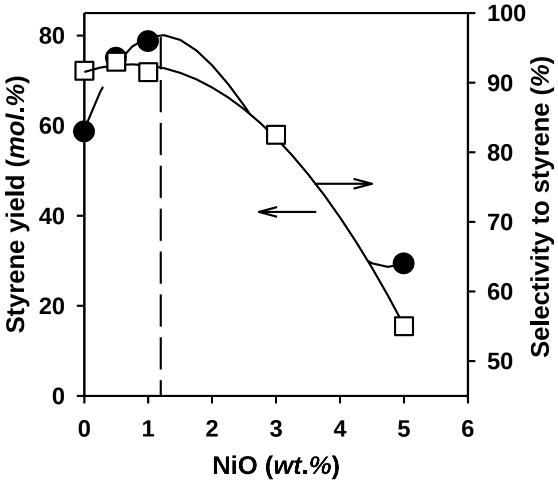

Fig. 3. Effect of NiO content on the activity and selectivity of 2 wt.% Na_2O - x wt.% NiO – 10 wt.% V_2O_5/γ-Al_2O_3 catalysts in the reaction of ethylbenzene dehydrogenation

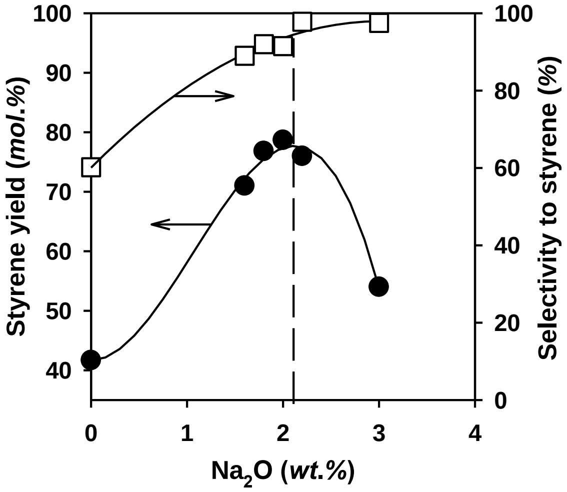

Fig. 4. Effect of Na_2O content on the activity and selectivity of x wt.% Na_2O - 1 wt.% NiO – 10 wt.% V_2O_5/γ-Al_2O_3 catalysts in the reaction of ethylbenzene dehydrogenation

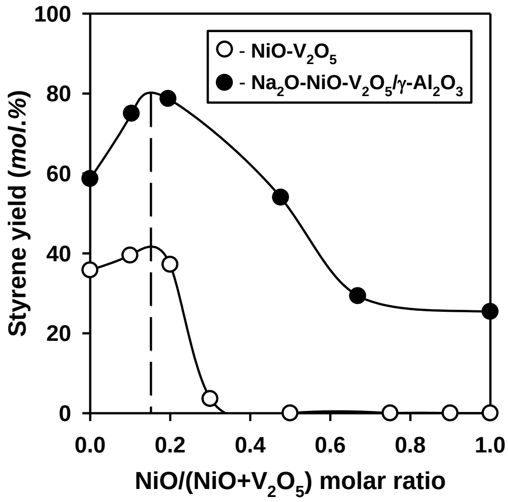

Fig. 5. Effect of NiO/(NiO + V_2O_5) molar ratio on the activity of unsupported NiO-V_2O_5 compositions and supported 2 wt.% Na_2O –(NiO + V_2O_5 = 11 wt.%)/γ-Al_2O_3 catalysts in the reaction of ethylbenzene dehydrogenation

A comparison of the XRD data with the dehydrogenation activities of binary NiO-V_2O_5 catalysts shows (see Table 1 and Fig. 5) that only bulk V_2O_5 phase exhibited dehydrogenating properties in the unsupported NiO-V_2O_5 catalysts; other phases present in the NiO-V_2O_5 samples (nickel vandates, NiO) catalyzed mostly the reactions of ethylbenzene cracking and dealkylation. The same explanation can probably be applied to catalytic behavior of γ-alumina supported NiO-V_2O_5-based samples (Fig. 5). It is worth to note that γ-Al_2O_3- and 2 wt.% Na_2O/γ-Al_2O_3 samples, as well as x wt.% NiO/γ-Al_2O_3- and 2 wt.% Na_2O - x wt.% NiO/γ-Al_2O_3 catalysts with low NiO contents (x ≤ 5 wt.%), possessed very low dehydrogenation activities.

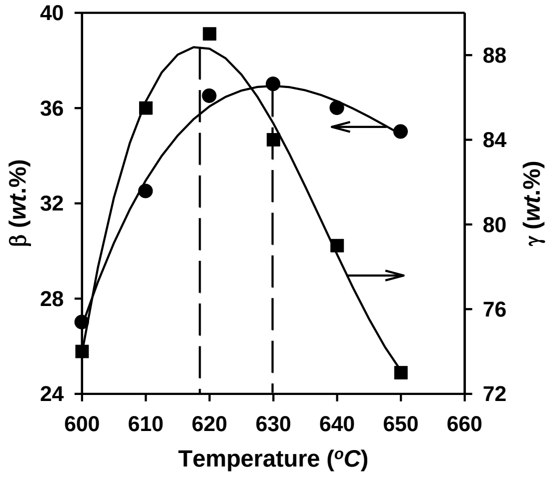

Fig. 6. Effect of temperature of dehydrotreatment process on the yield of vinyltoluenes per passed (beta) and converted (gamma) ethyltoluenes

Operating conditions:
Laboratory flow catalytic setup;
$LHSV_{C_9}$ = 0.3 h^{-1}; H_2O/feed mass ratio ~ 4:1

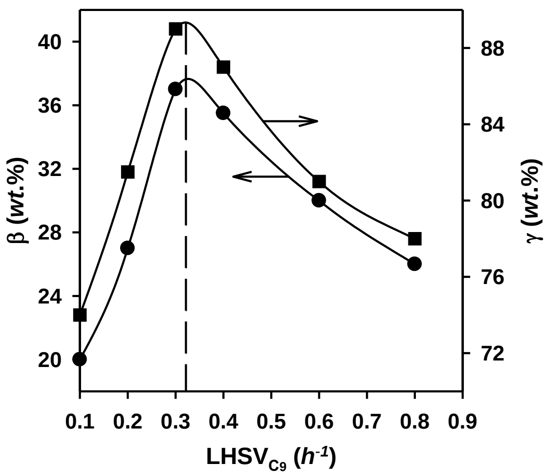

Fig. 7. Effect of $LHSV_{C_9}$ on the yield of vinyltoluenes per passed (beta) and converted (gamma) ethyltoluenes

Operating conditions:
Laboratory flow catalytic setup;
T = 630°C; H_2O/feed mass ratio ~ 4:1

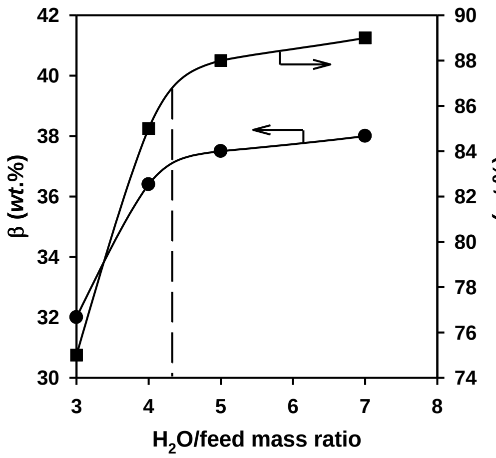

Fig. 8. Effect of H_2O/feed mass ratio on the yield of vinyltoluenes per passed (beta) and converted (gamma) ethyltoluenes during dehydrotreatment of ethyltoluenes-enriched C_9-fraction of hydrocarbons

Operating conditions:
Laboratory flow catalytic setup;
T = 630°C; $LHSV_{C_9}$ = 0.3 h^{-1}

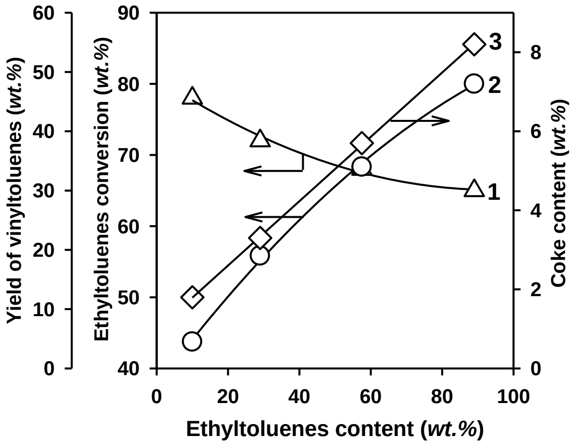

Fig. 9. Effect of ethyltoluenes content in mesitylene-containing feedstock on their conversion (1), yield of vinyltoluenes (2) and the amount of coke deposited on Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst (3)

Operating conditions:
Laboratory flow catalytic setup; T = 640°C;
$LHSV_{C_9}$ = 0.3 h^{-1}; H_2O/feed mass ratio ~ 4:1

Taking into account the above mentioned concentration dependences of styrene yields on the V_2O_5 and NiO contents in Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalysts (Figs. 2-4), these results point to the prevailing role of vanadium ions in the formation of active sites responsible for dehydrogenation activities of the catalysts under investigation. The role of nickel ions in these catalysts is restricted by only promotor functions.

Dependences of efficiencies of ethyltoluenes conversion on the parameters of dehydrotreatment process in the presence of 2 wt.% Na_2O -1 wt.% NiO – 10 wt.% V_2O_5/γ-Al_2O_3 catalyst (having the optimal chemical composition for ehydrogenation of alkylaromatic hydrocarbons) are depicted in Figures 6-8.

These results show that conversion of ethyltoluenes is the most efficient (yield of vinyltoluenes is of ~ 36÷38 wt.% per passed ethyltoluenes and of ~ 84÷89 wt.% per converted ethyltoluenes) under the following operating conditions: T ~ 620÷630°C, $LHSV_{C9}$ ~ 0.3÷0.4 h^{-1} and H_2O/feed mass ratio ≥ 4:1.

Results of special catalytic runs on dehydrotreatment of artificially prepared C_9 fractions containing different amounts of ethyltoluenes have shown that conversion of ethyltoluenes increased with decreasing concentrations of these impurities in hydrocarbon feedstocks (Fig. 9). However, technically accepted conversions of ethyltoluenes were achieved at their concentrations in C_9 fractions of ≤ 15 wt.% (see Fig. 9).

TABLE II. EFFECT OF DEHYDROTREATMENT CONDITIONS ON THE EFFICIENCY OF MESITYLENE RECOVERY FROM DEHYDRITREATED C_9-FRACTIONS OF VARIOUS ORIGINS[A]

Dehydrotreatment conditions[a]			**Yield of commercial mesitylene (b.p. ~ 164.6÷164.8°C) (wt.%)**	**Content of mesitylene in the commercial product (wt.%)**	**Efficiency of mesitylene recovery (% from its resources in the feedstock)**
T (°C)	**$LHSV_{C_9}$ (h^{-1})**	**H_2O/feed mass ratio**			
620	0.4	4:1	86.08	98.80	82.54
630	0.3	5:1	83.87	98.85	82.41
640	0.3	4:1	80.24	98.92	79.73
620[b]	0.4[b]	4:1[b]	88.32[b]	98.88[b]	82.29[b]
620[c]	0.4[c]	5:1[c]	86.55[c]	94.67[c]	77.84[c]

[a] Feed: narrow C_9 fraction distilled from light fractions of Kansk-Achinsk brown coal flash pyrolysis tar (b.p. ~ 164-165°C).

[b] Feed: narrow C_9 fraction distilled from a coke-oven solvent (b.p. ~ 161-166°C).

[c] Feed: narrow C_9 fraction distilled from gasoline reforming products (b.p. ~ 161-166°C).

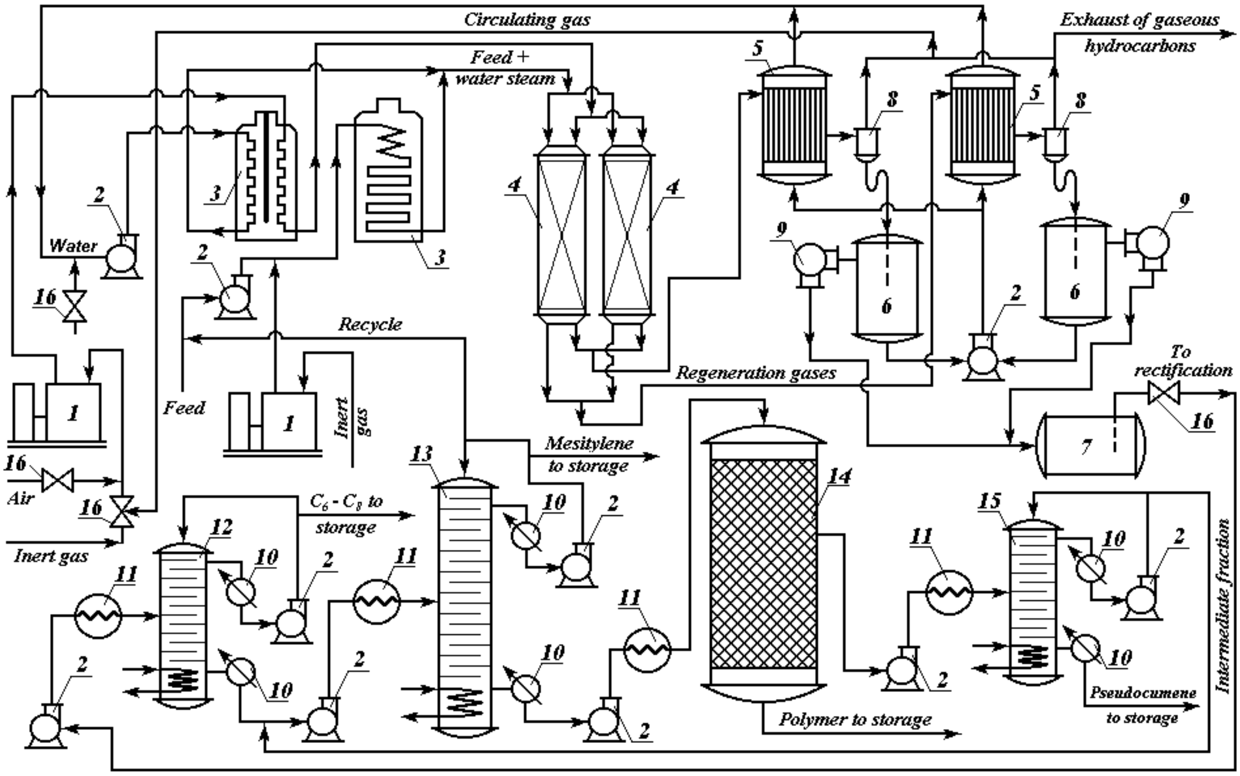

Fig. 10. Technological scheme for mesitylene production by dehydrotreatment method [4, 6]:

1 – gasholder; 2 – pump; 3 – tube furnace; 4 – reactor block; 5 – cooler; 6 – separator; 7 – dehydrogenate collection; 8 – gas separator; 9 – run-down box; 10 – flow meter; 11 - heater; 12,13,15 – distillation columns; 14 – polimerizator; 16 – valve.

The concentration dependence of ethyltoluenes conversion is due to thermodynamic features of hydrocarbon dehydrogenation processes (a *Le Chatelier* principle). From this point of view, coal-derived C_9-aromatics characterized by lowered concentrations of ethyltoluenes (≤ 10÷12 wt.%) are more preferable for pure mesitylene production than corresponding petroleum-derived C_9 fractions (where ethyltoluenes content often exceeds 20÷25 wt.%). Such a conclusion is confirmed by the experimental results on mesitylene recovery from dehydrotreated C_9 fractions which were obtained from hydrocarbon sources of various origins (see Table 2). As it can be expected, the best results were achieved during the dehydrotreatment of coal-derived C_9 fractions. In this case, yields of commercial mesitylene having > 98.80% purity were of ~ 82.5% from its resources in the initial feed (Table 2).

In practice, the above described process can be realized in a form of a product line almost analogous to that (with minimal modifications) at present used in the industrial process of ethylbenzene dehydrogenation to styrene. In addition to target hydrocarbon (mesitylene), a possibility of obtaining some other valuable products (polyvinyltoluene and pseudocumene) is also provided in the given scheme. This technological scheme adapted to mesitylene production (see Fig. 10) operates as follows [4, 6]. Hydrocarbon feedstock (C_9 fraction containing ~ 70-71% of mesitylene mixed with recycle), water and inert gas with a help of gasholders *1* and pumps *2* move through tube furnaces *3* into a fixed bed dehydrogenation catalyst reactor *4*. Dehydrogenate obtained after conversion of hydrocarbons in the reactor *4* goes to a dehydrogenate collector *7*, from which it through a heater *11* moves to a fractionating column with efficiency of 36 theoretical plates *12*. Distillate of this column is divided into two streams, one of them − commercial mesitylene of 98.5% purity – moves to storage, while the other one, in a form of recycle, is mixed with the initial C_9 fraction. Distillation residue is directed to a polymerizator *14*. Polyvinyltoluene formed in this polymerizator is removed to a warehouse, while the rest of polymerizate is fed to additional fractionating. Distillate of a column *15* (mesitylene mixed with some amounts of pseudocumene) returns to a column *13*, while distillation residue (pure pseudocumene) is directed to storage [4, 6].

Table 3 lists comparative performance characteristics for various methods of pure mesitylene recovery from technical mesitylene-containing fractions. Analysis of these data suggests that dehydrotreatment process is a fairly efficient, economical and relatively simple technically method for commercial mesitylene production. Among other undoubted advantages of the dehydrotreatment method, lack of needs in any deficient and toxic reagents for conducting technological operations and possibility of production (along with mesitylene) of some additional commercial products should be noted. This method allows one to maximally fully use the resources of mesitylene-containing feedstocks, and, thus, it can be considered as quite competitive process from the standpoint of industrial application.

TABLE III. COMPARATIVE PERFORMANCE CHARACTERISTICS FOR VARIOUS METHODS OF PURE MESITYLENE RECOVERY FROM TECHNICAL MESITYLENE-CONTAINING FRACTIONS

Characteristics	**Sulfidation-hydrolysis [16]**	**Complexing with DNBA[a] [17]**	**Izomerization-disproportionation [18]**	**Alkylation-dealkylation [4]**	**Hydrogenation-dehydrogenation [19]**	**Dehydrotreatment**	
						Cr-Mo[b] [6]	**Ni-V[c]**
Yield of commercial mesitylene (of ≥ 97.5% purity), % from its resourses in the feedstock	64.5	72÷80	60÷67	71.5	70÷75	78	82.5
Content in commercial mesitylene produced, wt.%:							
Mesitylene	97.7	99÷99.5	98.45÷98.81	98.32	99.17	98.73	98.95
Saturated hydrocarbons	1.1	no	0.84÷1.01	0.22	no	0.03	no
m- + *p*-Ethyl-toluenes	0.7	not determined	0.06	not determined	0.19	0.80	0.75
o-Ethyltoluene	not determined	not determined	0.14	not determined	not determined	0.44	0.30
Pseudocumene	0.5	not determined	0.15	1.46	0.64	no	no
Mesitylene losses (wt.%)	no data	no data	no data	no data	6÷7	2÷3	2÷3
Relative manufacturing cost of 1 ton of mesitylene[a]	1.00	no data	0.81	0.71	0.58	0.62	0.87

[a] DNBA = 3,5-Dinitrobenzoic acid.
[b] Dehydrotreatment in the presence of Na_2O-Cr_2O_3-MoO_3/γ-Al_2O_3 catalyst.
[c] Dehydrotreatment in the presence of Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst (results from this work).

IV. CONCLUSION

By analyses of concentration dependences of dehydrogenation activities of Na_2O-NiO-V_2O_5/γ-Al_2O_3 samples with various contents of supported components and with various NiO/(NiO+V_2O_5) molar ratios, the optimal chemical composition of NiO-V_2O_5-based catalyst for dehydrogenation of alkylaromatic hydrocarbons has been chosen (wt.%: V_2O_5 – 10; NiO – 1; Na_2O – 2; γ-Al_2O_3 – 87). It has been found that for both unsupported and γ-alumina supported NiO-V_2O_5 compositions with various ratios of nickel (II) and vanadium (V) oxides, dehydrogenation activity maxima were observed at NiO/(NiO+V_2O_5) molar ratios ~ 0.15. Taking into account phase and chemical compositions of the given samples, these results suggest that dehydrogenation activities of the catalysts studied are due to predominantly vanadium oxide species, while the role of nickel ions in them is restricted by only promotor functions.

To achieve maximally deep conversion of ethyltoluenes to vinyltoluenes during the dehydrotreatment of mesitylene-containing fractions distilled from coal pyrolysis products, the catalytic process should be conducted in the presence of

Na_2O-NiO-V_2O_5/γ-Al_2O_3 catalyst at T ~ 620-630°C, $LHSV_{C9}$ ~ 0.3-0.4 h^{-1} and H_2O/feed mass ratios ≥ 4:1. In this case yield of vinyltoluenes is of ~ 36÷38 wt.% per passed ethyltoluenes and is of ~ 84÷89 масс.% per converted ethyltoluenes.

A method for producing commercial mesitylene by dehydrotreatment of C_9-fractions of aromatic hydrocarbons obtained from coal pyrolysis products to remove ethyltoluene impurities contained in them, has been proposed. A technological scheme of this process is described, which comprises catalytic treatment of C_9 fractions of hydrocarbons over 2 wt.% Na_2O – 1 wt.% NiO – 10 wt.% V_2O_5/γ-Al_2O_3 catalyst in the presence of water steam, followed by two-step fractionation of the dehydrogenate separated from water. An advantage of using coal-derived mesitylene-containing fractions, compared to petroleum-derived ones, as feedstocks for the given process, has been emphasized. In practice, this process can be realized in a form of a product line almost analogous to that at present used in the industrial process of ethylbenzene dehydrogenation to styrene. Relative simplicity, feasibility, good quality of commercial mesitylene produced (of ≥ 98.8% purity) combined with high efficiency of its recovery from C_9 fractions of hydrocarbons (up to 82.5% from its resources in the feedstock), are the essential features of the technology proposed.

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