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# Production of Styrene by Dehydrogenation of Ethylbenzene
# on a [Re, W]/γ-Al₂O₃ (K, Ce)/α-Al₂O₃ Porous Ceramic Catalytic Converter

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This paper presents the results of a study on the the particularities of the process of dehydrogenation of ethylbenzene to styrene over an original [Re,W]/γ-Al₂O₃(K,Ce)/α-Al₂O₃ porous ceramic catalytic converter, obtained by self-propagating high-temperature synthesis and the sol-gel method. It was found that, over this converter, the output of styrene, with a ~ 100% selectivity to liquid products, is ~ 23 times higher than that over the same conventional bulk catalysts. Further, after 6 hours of reaction, the degree of carbonization of the converter does not exceed 5 wt.%, while it is XX wt.% over the corresponding unshaped catalyst.

*Keywords:* heterogeneous catalysis; porous ceramic catalytic converter; rhenium catalysts; self-propagating high-temperature synthesis; ethylbenzene dehydrogenation; monomer synthesis; styrene production.

*Abbreviations:* ETB – ethylbenzene; ABS – acrylonitrile-butadiene-styrene; SAN – styrene-acrylonitrile; SHS - self-propagating high-temperature synthesis; PCSPA - peat coal of sulfur-potassium activation; GFR - gas flow regulator; MCU - model control unit; MTC - microprocessor temperature controller; PT – pressure transducer; EP – excessive pressure; TC – thermocouple; GC - gas chromatography; GLC - gas-liquid chromatography; GC-MS - gas chromatography-mass spectrometry; FID - flame ionization detector; TCD - thermal conductivity detector; TEM-EDS - transmission electron microscopy with energy dispersive X-ray spectroscopy; XPS - X-ray photoelectron spectroscopy.

**Introduction**

Styrene is well known as the most important monomer used to produce numerous types of polymers such as polystyrene, foamed plastics, styrene-modified polyesters, ABS or SAN [1]. Currently, the global production of styrene is over 30 million tons per year [2].

The main method for the industrial production of styrene from the 30's of the twentieth century to the present time consists on dehydrogenation of ethylbenzene over iron oxide catalysts.

The reaction of dehydrogenation of ethylbenzene is endothermic ($\Delta H = 124$ kJ.mol$^{-1}$) and proceeds with an increase in volume:

$$C_6H_5-CH_2-CH_3 \longrightarrow C_6H_5-CH=CH_2 + H_2 \qquad (1)$$
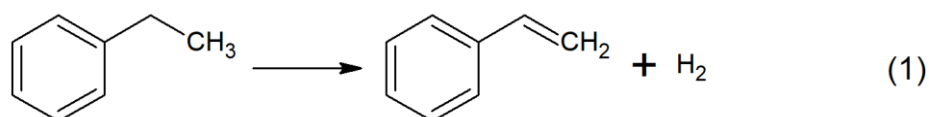
The apparent activation energy of the ethylbenzene dehydrogenation process is quite high (152 kJ/mol). It is therefore carried out at a temperature of about 600 °C. According to the Le Chatelier-Brown principle, an increase in the conversion of ethylbenzene is also promoted by a decrease in its initial partial pressure. To this end, the industrially conducted process includes dilution of ethylbenzene with water vapor with a molar ratio of $H_2O \div ETB = (15 - 17) \div 1$, the total pressure being maintained close to the atmospheric one.

The main problem of the industrial synthesis of styrene is that it is accompanied by numerous side reactions of formation of ethylbenzene conversion products, such as toluene, benzene, ethane, methane and carbon oxides, which significantly reduce the productivity of facilities for its preparation and complicate the subsequent purification stage [3]. Therefore, the main tasks related to intensification of the process of dehydrogenation of ethylbenzene to styrene are to improve the catalysts and to optimize the technological parameters and designs of existing equipment.

A large number of serious studies of a number of reputable world scientific schools have been devoted to the search for solutions to such issues, with works on both theoretical and applied aspects, dealing with reactors modeling [4], development of kinetic models [5], process parameters studies [6, 7] and with the synthesis of original catalytic systems [8-10]. However, the practical possibilities of the currently proposed solutions are still very limited.

Development of new types of catalytic reactors based on porous ceramic catalytic converters is considered to be a promising way to increase the efficiency of dehydrogenation processes [11]. This approach can make it possible to intensify the course of a dehydrogenation reaction and increase the selectivity of the process to the target product, mainly by reducing the overall energy requirements of the chemical conversion (as compared to traditional reactors with a stationary granular catalyst bed) due to improved heat and mass transfer in a highly porous

medium of a catalytic converter. The latter, due to the forced diffusion of substrate molecules in a spatially limited pore volume and a high ratio of catalytic surface area to pore volume, enables an increase in such an important factor in catalysis that represents the frequency of stochastic collisions of substrate molecules with pore walls modified by catalytically active components [12].

The effectiveness of the method presented in this paper is confirmed by previous studies on the high-speed production of hydrogen-containing gas in the processes of carbon dioxide, steam and mixed reforming of raw materials of fossil, synthetic and biological origin, such as methane, dimethyl ether and fermentation products [13-15], and in experiments on dehydrogenation of propane, butylene and *iso*amylene fractions to propylene, *1,3*-butadiene and isoprene, respectively [16, 17]. Another important factor that allows improvement in industrial technologies of basic organic synthesis is the prospect of using a catalytic converter as a replicable element of a new type of cassette reactors, which greatly simplifies the stages of loading and unloading of large volumes of catalysts, and also significantly increases the safety of the process.

## 1. Experimental

### 1.1 Synthesis of a porous catalytic converter for dehydrogenation of ethylbenzene to styrene

### 1.1.1 Obtaining of a tubular porous ceramic support based on $\alpha$-$Al_2O_3$

As the first stage of preparation of the catalytic converter using self-propagating high-temperature synthesis tubular porous ceramic support based on $\alpha$-$Al_2O_3$ is obtained, with one of its ends being plugged to provide "forced" diffusion of gases through the working surface of the cylinder from the outer wall to the inner wall (Fig. 1). On the other extremity it is equipped with a clamping nut for tight connection of the support to the reactor through a graphite gasket (not shown).



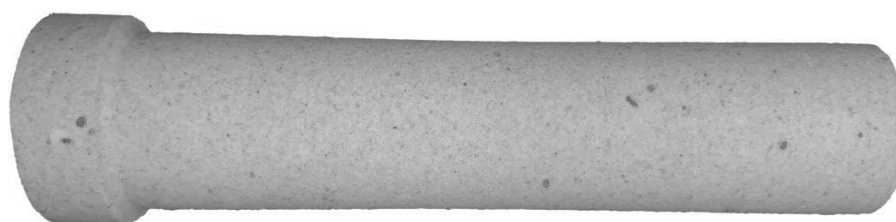Fig. 1. Tubular porous ceramic support based on $\alpha$-$Al_2O_3$.

Geometrical dimensions of the tubular support are as follows: total length – 137 mm; working area length – 120 mm; outer tube diameter – 25 mm; wall thickness – 7 mm.

The size of the open pores of the tubular porous ceramic support was determined by a capillary displacement model based on Laplace formula for the "model of cylindrical pores" using

a mercury porometer and the "bubble" method [18]. The diameter of the open pores of the support was from 1 to 3 μm. The porosity measured by hydrostatic weighing was more than 50%.

A large-fraction $\alpha$-$Al_2O_3$ powder of electrocorundum white with a particle size of 100 μm ("Litprom" LLC) was used as a raw material for the synthesis of the support.

In order to increase the mechanical strength of the support and its resistance to high temperatures, some powdered additives of eutectic composition were introduced into the initial $\alpha$-$Al_2O_3$ powder, namely magnesium oxide ("Krasny Khimik" chemical reagent factory, IS 4526-75) and silicon carbide in the following ratio: α-$Al_2O_3$ – 90 wt. %; MgO – 3 wt. %; SiC – 7 wt. %. In the course of the SHS synthesis, these compounds form active $SiO_2$ that binds $\alpha$-$Al_2O_3$ particles to each other due to their transformation into mullites, indialite ($Mg_2Al_4Si_5O_{18}$) and spinel ($MgAl_2O_4$) [19].

These powders were mixed in a ball mill for 1 h; then the as-obtained mixture underwent single-action compression at 30 – 90 MPa and sintering at 1300 – 1450 °C in air for 1 h followed by cooling to room temperature for 2 hours.

A liquid phase of eutectic composition is formed during sintering at temperature in the range of 1300 – 1450 °C.It contains magnesium oxide and silicon carbide in the form of clinoenstatite. This latter wets $Al_2O_3$ particles and thus forms a strong porous support frame. Hereinafter, for simplicity of writing catalyst compositions, the tubular ceramic support will be referred to as "$\alpha$-$Al_2O_3$" (or just "support"), without mentioning the additives.


### 1.1.2 Modification of the synthesized support with a Re-W-containing catalyst system

Considering the published data, an original polymetallic system containing rhenium-tungsten catalyst components deposited separately on the support [20] was chosen as the object of the present study of dehydrogenation of ethylbenzene to styrene. Note that we e will further investigate the subject of the impact of co-precipitation of catalytic components on dehydrogenation processes in subsequent works.

The catalytic system was formed on the surface of the pore walls of the support by molecular layering of colloidal solution of precursors. Preliminarily, in order to increase the inner surface of the pores, an intermediate $\gamma$-$Al_2O_3$ layer was designed. To that purpose, a colloidal solution of a sol consisting of 0.03 mol. % $H_2O$, 1.5 mol/l Al $(OPr^i)_3$ (98%, "Acros Organics"), 1.5 mol of acetylacetone (98%, "Fluka)" in toluene ("Ekos-1", IS 5789-78) was deposited by pumping through the pores of the support. Then, the modified porous ceramic support was dried under a stream of air in a furnace at 120 °C for 1 h, before being thermally treated in the heat shock mode at 500 °C for 30 min. The amount of precipitated $\gamma$-$Al_2O_3$ was estimated by the increase in weight of the sample. The impregnation stage was repeated four times until the weight gain

reached 4 – 5 wt. %. Then, in order to suppress side reactions of styrene polymerization, $K_2O$ and $CeO_2$ were introduced by subsequent impregnation of the converter with an aqueous solution of $K_2CO_3$ and cerium nitrate.

Then, active rhenium-tungsten-containing components from hydroalcoholic solutions of the corresponding $NBu_4ReO_4$ and $(NH_4)_6W_{12}O_{39} \cdot H_2O$ complexes were deposited. Formation of Re (7+) and W (6+) oxides was carried out by calcination of the impregnated sample in a muffle furnace under air stream at various temperatures: at 500 °C for 2 h, at 600 °C for 2 h, at 800 °C for 1 h. The amount of deposited components was determined by the weight gain of the sample after the stages of heat treatment.

The initial weight of the support was 108.63 g. The respective contents of the introduced components of the modified support are given below, wt. %:

| $K_2O$ | $CeO_2$ | $Re_2O_7$ | $WO_3$ | $\gamma$-$Al_2O_3$ | $\alpha$-$Al_2O_3$ (support) |
|--------|---------|-----------|--------|--------------------|------------------------------|
| 0.11   | 0.05    | 0.16      | 0.08   | 4.68               | 94.92                        |

Hereinafter, for simplicity, the [Re,W]/$\gamma$-$Al_2O_3$(K,Ce)/$\alpha$-$Al_2O_3$ modified support will be referred to as the "converter".

## 1.2 Configuration of the laboratory facility and flow-type catalytic reactor

Dehydrogenation of ethylbenzene to styrene on the developed [Re,W]/$\gamma$-$Al_2O_3$(K,Ce)/$\alpha$-$Al_2O_3$ catalytic converter was studied using an original laboratory facility and a flow-type reactor, their configuration being shown in Fig. 2 and 3.
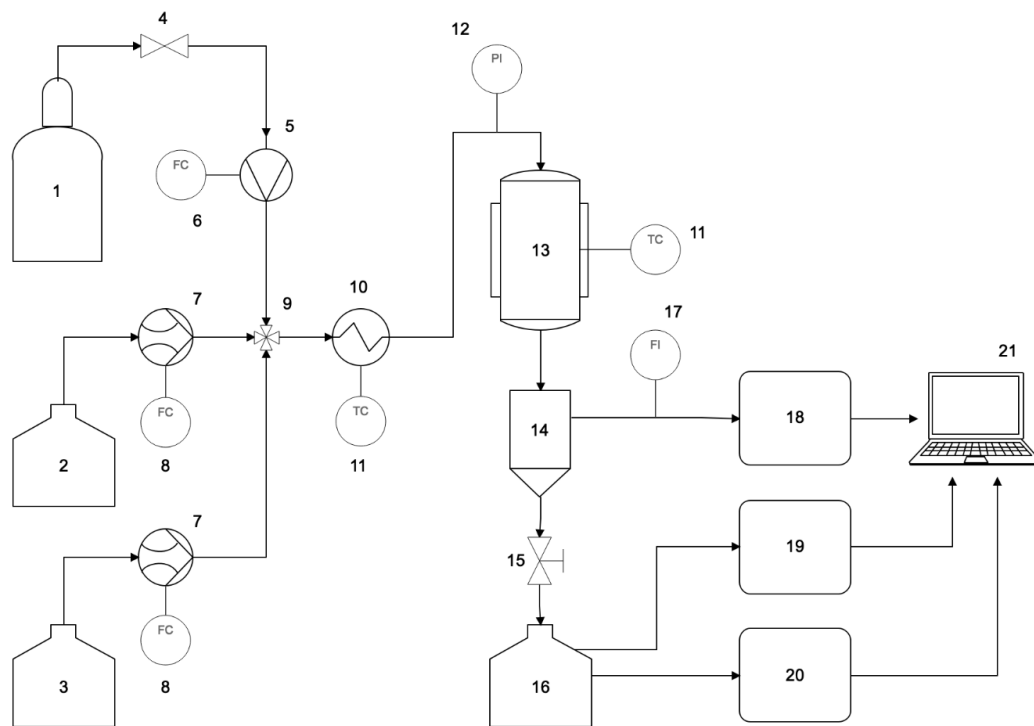
Fig. 2. Configuration of a laboratory facility for dehydrogenation of ethylbenzene to styrene. Designations: 1 – argon cylinder; 2 – ethylbenzene tank; 3 – distilled water tank; 4 – gas pressure regulator; 5 – gas flow regulator; 6 – mass flow meter/controller for gases; 7 – flow controller for liquids; 8 – indicator of flow controller for liquids; 9 – gas-liquid flows mixing connector; 10 – evaporator; 11 – temperature processor; 12 – pressure sensor; 13 – catalytic reactor;  14 – gas liquid separator; 15 – gate valve; 16 – flow receiver; 17 – gas flow indicator; 18 – GC; 19 – GC-MS; 20 – GLC; 21 – data analysis workstation.
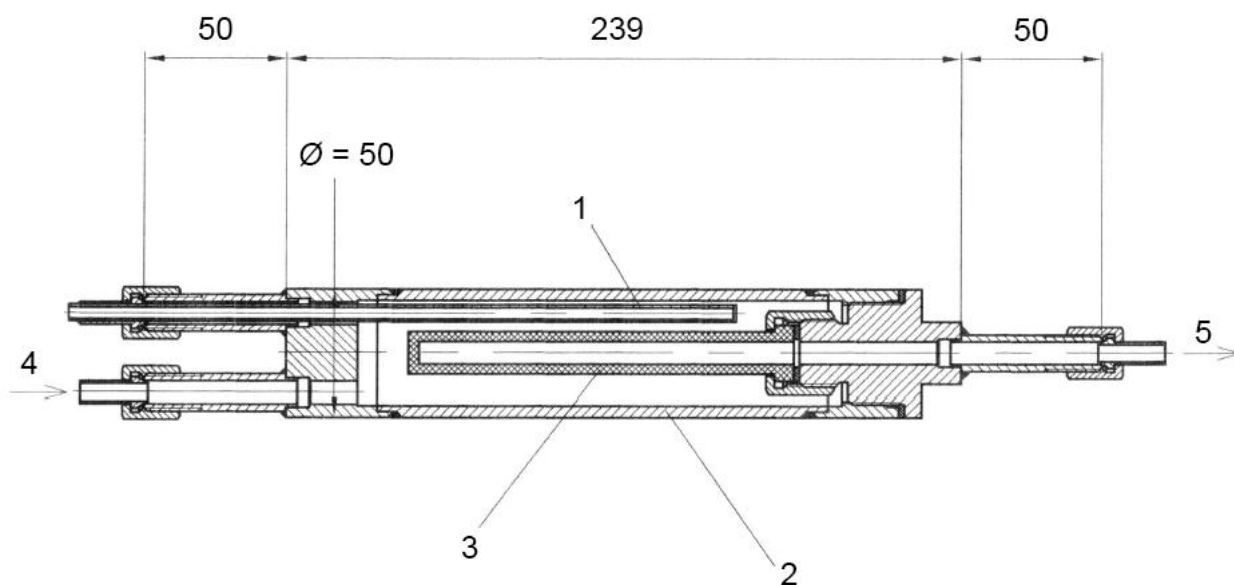


Fig. 3. Configuration of a flow-type reactor with an installed catalytic converter (the dimensions

are set in mm). Designations: 1 – thermocouple pockets; 2 – reactor body; 3 – tubular catalytic converter; 4 – feeding of raw materials; 5 – removal of reaction products.

### 1.3 Experimental method

Prior to experiments of dehydrogenation of ethylbenzene to styrene using the above described laboratory facility, a catalytic converter was pre-installed in the reactor (position 13 in Fig. 2), the reactor itself was assembled and sealed and then mounted on the facility. Then, a pressure test for the whole system with argon was carried out at X MPa during 15 min. In order to prevent undesired oxidation of the deposited catalytically active components of the converter with residual atmospheric oxygen, the reactor with the installed sample was heated to the onset temperature of the process (and then to each reference point in increments of 25 °C in the range of 500 – 650 °C) under an argon stream (99.998%, IS 10157-79) supplied from the gas cylinder (1) through the regulator (4). The argon flow rate was set at 2.5 L/h and was controlled with an electronic GFR "Eltochpribor MCU-1" (5). Upon reaching the required temperature, the supply of argon was ceased, and a separate supply of raw materials (ethylbenzene, "REAHIM", TS 6-09-2786-73) and a diluent (distilled water) from the built-in tanks (2) and (3) was started using the "High Pressure Pump 5001" flow controllers for liquids (7). The volumetric feed rates of the substrates were set at 0.1 and 0.2 mL/ min, respectively, to ensure a molar ratio of $H_2O \div ETB = 14$ and a partial pressure of ethylbenzene of ~ 0.01 MPa. Mixing of fluid flows occurred in the connector (9). In order to homogenize the total liquid flow directed to the reactor, it was previously evaporated in the coil-type evaporator (10) at a temperature of 200 °C. The temperature of the evaporator was controlled with a microprocessor temperature controller "OVEN MTC-210" (11). The steam-gas water-organic mixture stream was then introduced in the catalytic reactor (13). For heating of the reactor furnace and regulation of the temperature an "OVEN MTC-251" temperature processor (Thermocouple TC-0198, chromel-alumel (K)) (11) was used. The pressure in the reactor was measured with an "OVEN PT100-EP" pressure meter and indicated by an "OVEN 2MTC0" device (12). Raw materials were fed to the catalytic reactor at each temperature reference point for 1 h in order to establish steady conditions of the dehydrogenation process and to ensure collection of reaction products in the gas and liquid receivers of the facility in quantities necessary for conducting GC, GLC, and GC-MS analyzes. Before gas sampling, the outlet pipelines connected to the receiver were purged with the product gas for 15 minutes. The rate of the product gas stream taken to the receiver was measured using a "Sinagawa DC-2C-M" gas meter (17). The selected gas sample was analyzed by gas chromatography to determine the content of inorganic ($H_2$, CO, $CO_2$) and hydrocarbon ($C_1 – C_5$) gases on "Kristallux-4000M" chromatographs (18) equipped with FID and TCD. Output liquids were separated from gas and concentrated in the gas-

liquid separator cooled by tap water (14) throughout the entire time of each temperature reference point, and then, by opening the gate valve (15), they were poured into the sampler (16). Next, the volume of the sample was measured, the aqueous layer was separated from the organic one, and then the organic phase was analyzed by chromatography-mass spectrometry (qualitatively) (19) and gas-liquid chromatography (quantitatively) (20). The data obtained from analytical instruments were processed using special software on the data analysis workstation (21). Upon completion of the experiment, the catalytic reactor was cooled to room temperature in an argon atmosphere in order to prevent undesired oxidation of the catalyst.

## 1.4 Methods of analysis of the reaction products

The contents of hydrogen, carbon oxides and methane in the reaction products were determined by gas chromatography on a "Cristallux-4000M" chromatograph ("Meta-Chrom", Russia), with a katharometer as a detector and high-purity argon (99.998% IS 10157-79) as a carrier gas with a consumption rate of 10 mL/min; the adsorption packed column size was 1 m × 3 mm. As a column filler, PCSPA with a particle size of 0.2 - 0.3 mm was used. The temperature of the column, detector and evaporator was 120 °C. The gas concentrations were determined using calibration curves using a special software NetChrom v2.1.

Hydrocarbon gases $C_1 – C_5$ were identified on a "Cristallux-4000M" chromatograph ("Meta-Chrom", Russia) using FID, the carrier gas being helium (TS 0271-001-45905715-02). The following gas consumption rates were determined: helium - 30 mL/min; hydrogen - 35 mL/min; air - 300 mL/min. For the analysis a "HP-PLOT/$Al_2O_3$" chromatographic column ("Agilent Technologies", USA, 50 m × 0.32 mm, film thickness being 8.0 μm) was used. The temperatures of the column, detector and evaporator were 120 °C, 230 °C and 250 °C, respectively. The product concentrations were determined with calibration curves using a special software NetChrom v2.1.

The liquid organic reaction products were identified by GC-MS and GLC. The GC-MS analysis was performed using a "Thermo Focus DSQ II" gas chromatograph/mass spectrometer equipped with a quadrupole mass analyzer, the electron energy being 70 eV. The voltage on the electron multiplier was 1244 V. The temperature of the ion source was 280 °C. The interface temperature was 280 °C. Detection was carried out in the mode of registration of the total ion current SIM (Selected Ion Monitoring).

The GLC analysis was carried out on a "Varian 3600" chromatograph ("Varian Chromatography System", USA), equipped with an FID, a "Chrom Tech SE-30" capillary column, 25 m × 0.25 mm, $D_f = 0.33$ μm. The temperature conditions were: 50 °C (5 min), 10 °C/min, 280

°C, $T_{\text{inj.}}$ = 250 °C; $P_{\text{inj}}$= 1 bar, split ratio1/200, helium as a carrier gas (TS 0271-001-45905715-02).

## 1.5 Structural analysis method

The structure of the catalytic converter material and the distribution of elements on its surface were studied using transmission electron microscopy with a "TEM TITAN Themis 300" instrument ("FEI", USA).

The surface was analyzed using X-ray photoelectron spectroscopy on an "Axis Ultra DLD" instrument ("Kratos Analytical Ltd.", UK) with AlK$\alpha$ monochromatic X-ray radiation (15 kV, 15 mA, 1486.6 eV). All the spectra were calibrated in energy using the position of the C1$s$ peak, which is corresponding to the C – C and C – H bonds at 284.8 eV.

## 1.6 Calculation method

### 1.6.1 Calculation of the chemical equilibrium constant

To simplify calculations of the chemical equilibrium of ethylbenzene dehydrogenation into styrene, the following assumptions were made: only dehydrogenation of ethylbenzene to styrene was taken into account, without consideration of any others side transformations, which were thus neglected. This was done due to the fact that the real process of dehydrogenation of ethylbenzene involves a variety of different reactions, for example irreversible such as pyrolysis, and therefore is not a process at the equilibrium anyway.

For the reaction written in the general form as:

$$\nu_1 B_1 + \nu_2 B_2 + \cdots = \nu_1' B_1' + \nu_2' B_2' + \cdots \tag{2}$$
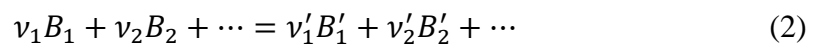
equilibrium constants $K_p$, $K_c$ и $K_x$ are interrelated as:

$$K_p = K_c (RT)^{\Delta \nu} = K_x P^{\Delta \nu} \tag{3}$$

where $\Delta \nu = \sum \nu_i' - \sum \nu_i$. Whence it follows that $K_p = K_c = K_x$, if $\Delta \nu = 0$ or $P = 1$ atm. Thus, the chemical equilibrium constant was calculated according to the equation:

$$K_p = e^{\frac{-\Delta_r G_T}{R \cdot T}} \tag{4}$$

Reference data for calculation of Gibbs energy were taken from [13].

### 1.6.2 Calculation of equilibrium reaction parameters

ethylbenzene    +    water vapor (inert)    =    styrene    +    hydrogen
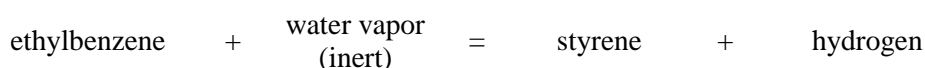
*Stoichiometric coefficients of the chemical equation ($\nu_i$)*

| 1 | 0 | 1 | 1 | |

*Mole fractions of the components of the reaction system at the time-reference point* $(x_i)$

| $1 - z$ | $z$ | $0$ | $0$ | $\sum x_i = 1$ |

*Equilibrium degree of conversion of the components of the reaction system* $(\bar{n}_i)$

| $(1 - z) \cdot (1 - \bar{y})$ | $z$ | $(1 - z) \cdot \bar{y}$ | $(1 - z) \cdot \bar{y}$ | $\sum \bar{n}_i = 1 + \bar{y} \cdot (1 - z)$ |

*Equilibrium mole fractions of the components of the reaction system* $(\bar{x}_i)$

| $\dfrac{(1 - z) \cdot (1 - \bar{y})}{1 + \bar{y} \cdot (1 - z)}$ | $\dfrac{z}{1 + \bar{y} \cdot (1 - z)}$ | $\dfrac{(1 - z) \cdot \bar{y}}{1 + \bar{y} \cdot (1 - z)}$ | $\dfrac{(1 - z) \cdot \bar{y}}{1 + \bar{y} \cdot (1 - z)}$ | $\sum \bar{x}_i = 1$ |

The equilibrium constant equals to:

$$K_x = \frac{\bar{x}_{B_1'}^{\nu_1'} \cdot \bar{x}_{B_2'}^{\nu_2'} \cdots}{\bar{x}_{B_1}^{\nu_1} \cdot \bar{x}_{B_2}^{\nu_2} \cdots} = \prod \bar{x}_{A_i}^{\nu_i} = \frac{[\text{styrene}]^1 \cdot [\text{hydrogen}]^1}{[\text{ethylbenzene}]^1} = \frac{(1-z) \cdot \bar{y}^2}{(1-\bar{y}) \cdot [1 + (1-z) \cdot \bar{y}]} \tag{5}$$

Then the equilibrium degree of conversion equals to (mole fraction):

$$\bar{y} = \frac{-\left(K_x - \frac{K_x}{1-z}\right) - \sqrt{(K_x - \frac{K_x}{1-z})^2 - 4 \cdot (-K_x - 1) \cdot \frac{K_x}{1-z}}}{2 \cdot (-K_x - 1)} \tag{6}$$

and the mole fraction of the reaction products in the mixture:

$$\bar{x}_{\text{styrene/hydrogen}} = \frac{(1-z) \cdot \dfrac{-\left(K_x - \frac{K_x}{1-z}\right) - \sqrt{(K_x - \frac{K_x}{1-z})^2 - 4 \cdot (-K_x - 1) \cdot \frac{K_x}{1-z}}}{2 \cdot (-K_x - 1)}}{1 + (1-z) \cdot \dfrac{-\left(K_x - \frac{K_x}{1-z}\right) - \sqrt{(K_x - \frac{K_x}{1-z})^2 - 4 \cdot (-K_x - 1) \cdot \frac{K_x}{1-z}}}{2 \cdot (-K_x - 1)}} \tag{7}$$

The content of water vapor in relation to ethylbenzene (mole fraction):

$$z = \frac{n_{H_2O}}{1 + n_{H_2O}} \tag{8}$$

Mole content of the components of the equilibrium reaction mixture are proportional to their mole fractions, so, excluding inert, their sum equals to (mole):

$$\sum \bar{x} = \bar{x}_{\text{styrene}} + \bar{x}_{\text{hydrogen}} + \bar{x}_{\text{ethylbenzene}} \tag{9}$$

Then, the equilibrium styrene output (for simplicity of understanding it is designated in Fig. 4 as "equilibrium content of styrene in the reaction products"), excluding inert, equals to (mol.%):

$$\bar{\eta}_{\text{styrene}} = \frac{\bar{x}_{\text{styrene}}}{\sum \bar{x}} \cdot 100\% \tag{10}$$

### 1.6.3 Calculation of the resulting parameters of the experiment

Conversion of ethylbenzene, mol. %:

$$y_{\text{ethylbenzene}} = \frac{n_{\text{styrene}}}{n_{\text{ethylbenzene}}} \cdot 100\% \tag{11}$$

where $n$ is the amount of the substance, mole.

Styrene output from a theoretically conceivable one, mol. %:

$$\chi_{\text{styrene}} = \frac{n_{\text{styrene}}}{\bar{n}_{\text{styrene}}} \cdot 100\% \tag{12}$$

where $n_{\text{styrene}}$ is a mole of styrene obtained in the experiment, and $\bar{n}_{\text{styrene}}$ is a mole of styrene calculated according to chemical equilibrium.

The yield of styrene in relation to the flowed ethylbenzene (designated in Fig. 4 as "experimental styrene content in the reaction products"), mol. %:

$$\eta_{\text{styrene}} = \frac{n_{\text{styrene}}}{n_{\text{ethylbenzene}}} \cdot 100\% \tag{13}$$

The yield of styrene in relation to the converted ethylbenzene (styrene selectivity of the process), mol. %:

$$S_{\text{styrene}} = \frac{n_{\text{ethylbenzene}}}{n_{\text{styrene}}} \cdot 100\% \tag{14}$$

Styrene output by a gram of the active component, l/(h·g$_{\text{act.comp.}}$):

$$\rho_{\text{styrene}} = \frac{V_{\text{styrene}}}{m_{\text{act.comp.}}} \tag{15}$$

where $V_{\text{styrene}}$ is a volumetric flow of the formed styrene, l/h, and $m_{\text{act.comp.}}$ is a total mass of the deposited active components (for those there were taken $Re_2O_7$ and $WO_3$), g.

## 2. Results and discussion

### 2.1 Dehydrogenation of ethylbenzene to styrene over a Re-W-contained catalytic converter

As a result of the study of ethylbenzene dehydrogenation to styrene on the $\alpha$-$Al_2O_3$ support and the [Re, W]/$\gamma$-$Al_2O_3$ (K, Ce)/$\alpha$-$Al_2O_3$ catalytic converter in the presence of water vapor taken in the molar ratio of $H_2O \div ETB = 14$ and the raw materials feed space velocity of ~1.4 h$^{-1}$, it was found that there is a great catalytic impact of low Re and W depositions on the surface of the $\alpha$-$Al_2O_3$ support (Fig. 4, 5). Optimum styrene formation temperature was 600 °C (Fig. 5). As it is seen in Fig. 5 and 6, at this temperature the conversion of ethylbenzene was ~ 44 mol. %, the styrene yield from theoretically conceivable was ~ 76 mol. %, the styrene content in the reaction products was ~ 33 mol. %, the styrene selectivity wass ~ 74 mol. %, and the styrene productivity was ~ 7.23 g/(h·g$_{\text{act.comp.}}$). It is important to note that in the temperature range of 500 – 625 °C, the

liquid by-products, such as benzene and toluene, were present as trace amounts in the condensed product mixture, which underlines the high styrene selectivity of the developed Re-W-containing catalytic converter. The degree of carbonization of the $[Re, W]/\gamma$-$Al_2O_3$ (K, Ce)/$\alpha$-$Al_2O_3$ catalytic converter within 6 hours of the experiment, determined by the gravimetric method, did not exceed 5 wt. %.

On the $\alpha$-$Al_2O_3$ single support at temperatures below 575 °C, ethylbenzene was primarily converted to carbon (Fig. 4). Styrene was only detected in trace amounts. Since the support by definition does not contain deposited active components, it is not possible to make a comparative assessment of the performance of styrene per gram of catalyst. However, in terms of volume performance of the ceramic tube, the styrene performance of the support was 3.2 times lower than that of the modified sample at 600 °C (40.63 *vs.* 129.62 L/(h·dm$^3$)) and 1.6 times lower at 625 °C (72.51 *vs.* 116.60 L/(h·dm$^3$)).

It was shown that, at temperatures below 600 °C, the rate of ethylbenzene dehydrogenation is not high enough and thus does not allow to obtain the amount of styrene, which then becomes at 600 °C under the given conditions applied to this converter, while at temperatures above 600 °C, the intensification of side conversions leads to an increase in the content of products of cracking and steam reforming of hydrocarbons in product gases (Table 1). This results in a decrease in styrene yield and selectivity, as well as in accelerated coking of the catalyst. At 650 °C, the proportion of side nonequilibrium conversions of ethylbenzene increases up to 100%.

According to the published data, the conventional industrial processes of dehydrogenation of ethylbenzene to styrene are carried out in two-section adiabatic reactors with large loads (up to 100 tons) of iron oxide catalysts containing up to 80 wt. % $Fe_2O_3$, at temperatures of 600 – 615 °C, a volumetric feed rate of 0.3 – 0.5 h$^{-1}$, a molar ratio of $H_2O$ ÷ ETB = 15 - 17 and a partial pressure of ethylbenzene of 0.08 MPa. The degree of conversion of ethylbenzene in this case is ~ 50 mol. %, styrene selectivity is ~ 90 mol. %, styrene yield to the flowed ethylbenzene is ~ 44 mol. %, styrene output is ~ 0.3 g/(h·g$_{act.comp.}$) [21-27].

Higher values of some process parameters achieved on industrial catalysts, as compared with the results obtained on the system we developed, probably result from the peculiarities of the kinetic control of the reaction, which will certainly be the subject of our further research.

Based on the obtained data, it can be concluded, that even at the current experimental stage the developed catalytic converters, containing small amounts of nanosized active particles of rhenium and tungsten (less than 0.5 wt.%) on the surface of a porous ceramic carrier, can successfully compete with existing industrial solutions, providing ~ 23 times more styrene output at lower costs per amount of the fed water and loaded catalyst. Such a great advantage of catalytic converters in comparison with traditional reactors with a granular catalyst bulk layer is likely to

be due to the improved heat and mass transfer of the reagent in a spatially limited pore volume of the converter, which is an assembly of nanoreactors. An increase in the transverse diffusion of substrate molecules in narrow sinuous channels of the converter leads to higher probability of their contact with the active surface of the catalyst, which can explain intensification of catalytic conversions and increasing resistance of the converter to coke formation [28].

Proceeding from our previous studies, one can consider the use of a palladium-containing membrane integrated in the outlet channel of the converter for simultaneous extraction of ultrapure hydrogen from the reaction zone [15] to be of particular interest. Thus, the use of catalytic converters in cassette-type hybrid reactors can stimulate creation of small-sized chemical plants, opening new paths for development of modern processes in petrochemistry.
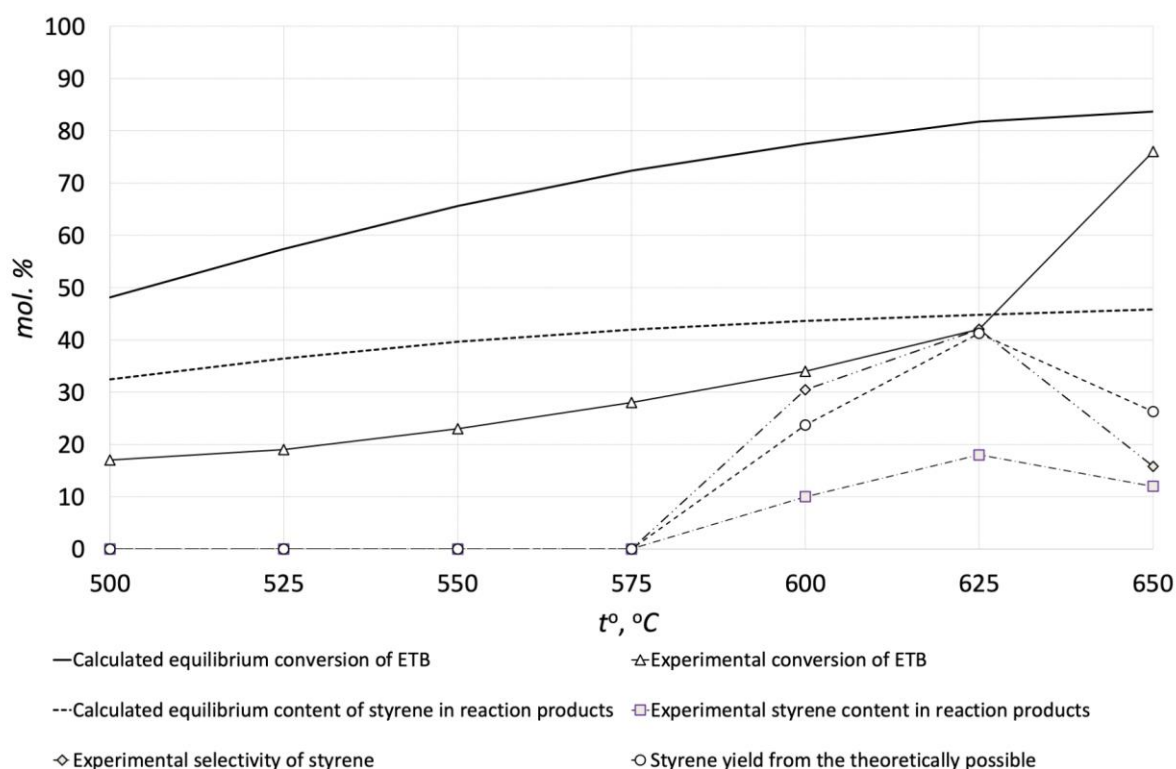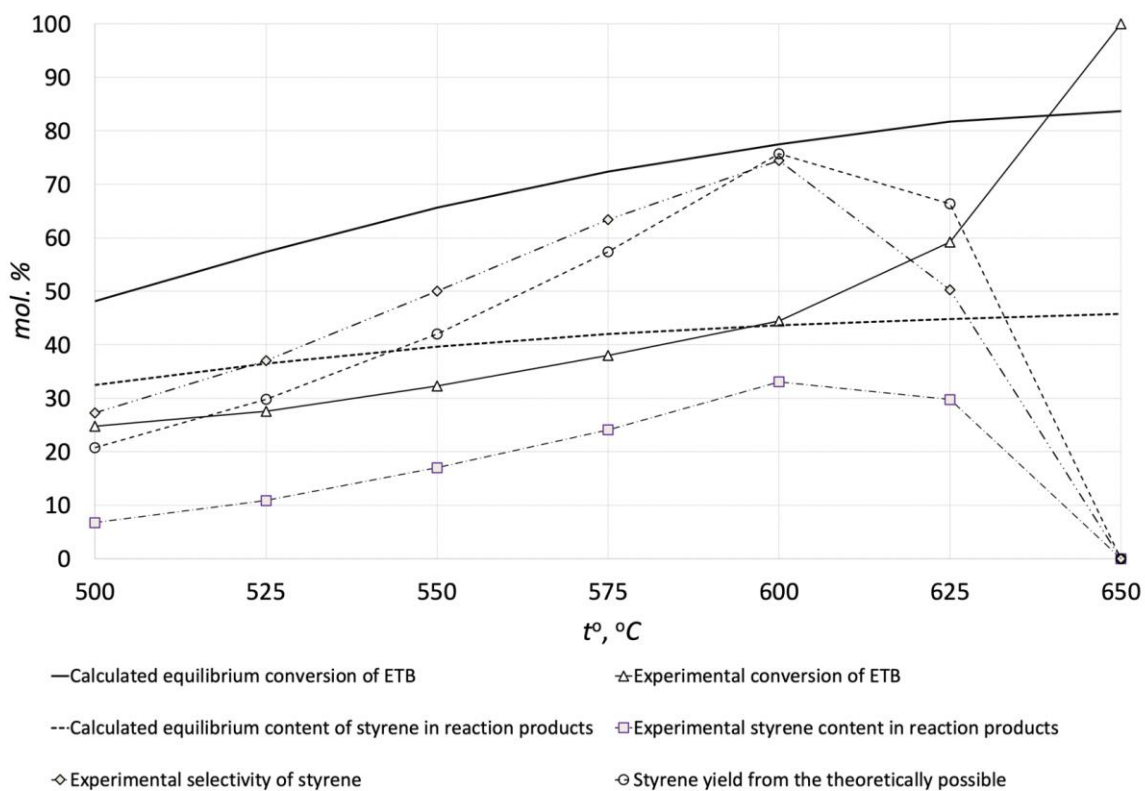


Fig. 4. Comparison of the calculated equilibrium and experimental temperature dependences of the main parameters of the process of dehydrogenation of ethylbenzene to styrene on the $\alpha$-Al$_2$O$_3$ support (blank test).

Fig. 5. Comparison of the calculated equilibrium and experimental temperature dependences of the main parameters of the process of dehydrogenation of ethylbenzene to styrene over the $[Re,W]/\gamma\text{-}Al_2O_3(K,Ce)/\alpha\text{-}Al_2O_3$ catalytic converter.
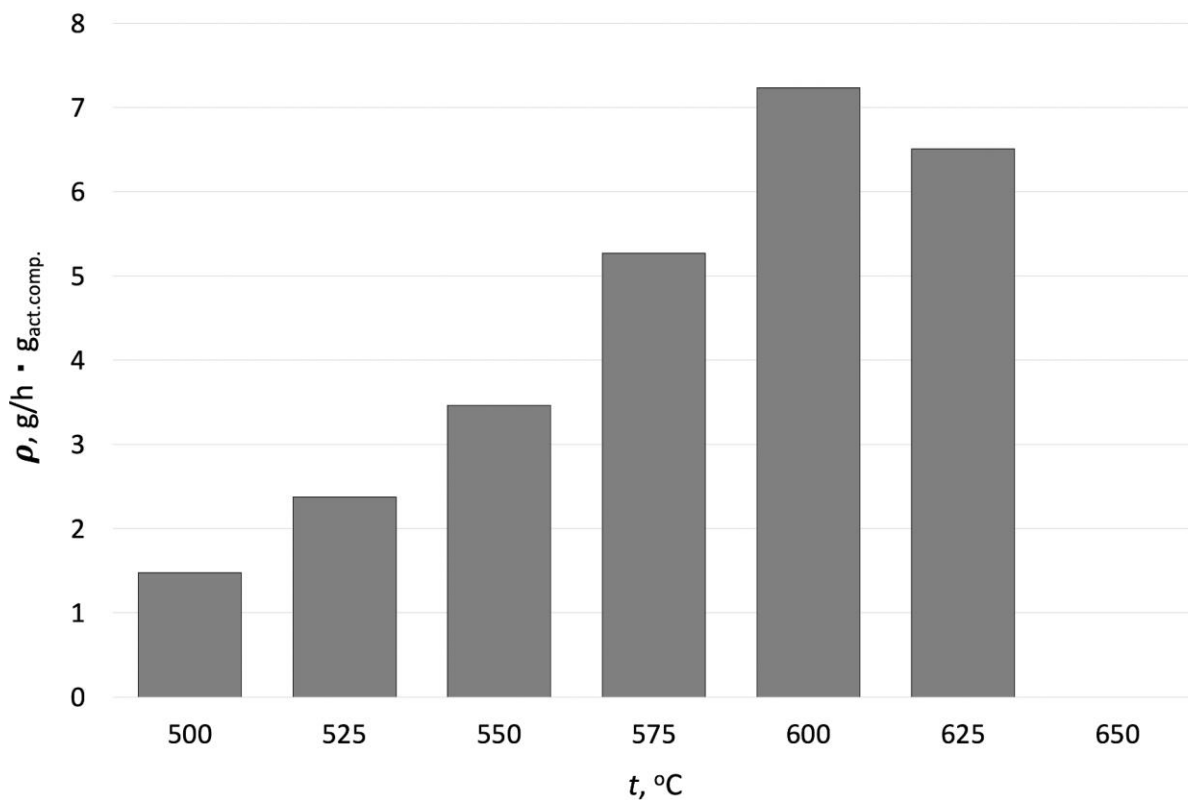


Fig. 6. Styrene output on a $[Re,W]/\gamma\text{-}Al_2O_3(K,Ce)/\alpha\text{-}Al_2O_3$ catalytic converter in the temperature range of 500 – 650 °C.

Tab. 1. The composition of product gases after dehydrogenation of ethylbenzene to styrene on a [Re,W]/$\gamma$-Al$_2$O$_3$(K,Ce)/$\alpha$-Al$_2$O$_3$ in a temperature range of 500 – 650 $^{\circ}$C, mol. %.

| $T$, $^{\circ}$C | H$_2$ | CO | CO$_2$ | CH$_4$ | C$_2$H$_6$ | C$_2$H$_4$ |
|---|---|---|---|---|---|---|
| 500 | 95.50 | 0.34 | 3.20 | 0.79 | 0.08 | 0.08 |
| 525 | 93.57 | 1.04 | 3.59 | 1.41 | 0.17 | 0.23 |
| 550 | 91.76 | 1.26 | 4.14 | 2.01 | 0.29 | 0.54 |
| 575 | 87.29 | 2.03 | 6.40 | 2.98 | 0.46 | 0.85 |
| 600 | 83.27 | 2.75 | 7.75 | 3.79 | 0.73 | 1.71 |
| 625 | 78.85 | 3.29 | 9.99 | 4.78 | 0.93 | 2.16 |
| 650 | 67.78 | 15.72 | 10.94 | 4.99 | 0.29 | 0.28 |

## 2.2 Studying of the evolution of the structure of the developed catalytic Re-W-containing converter in the course of dehydrogenating of ethylbenzene

As a result of TEM-EDS analysis of the fresh converter sample, a large number of individual atoms and groups of rhenium and tungsten atoms homogeneously distributed over the $\alpha$-Al$_2$O$_3$ surface were detected, while no atom agglomerations into nanoclusters were detected (Fig. 7 (a, b)). This fact counts in favor of the sol-gel method as an effective way to deposit evenly small amounts of highly dispersed atomic size catalysts over shaped tubular supports.
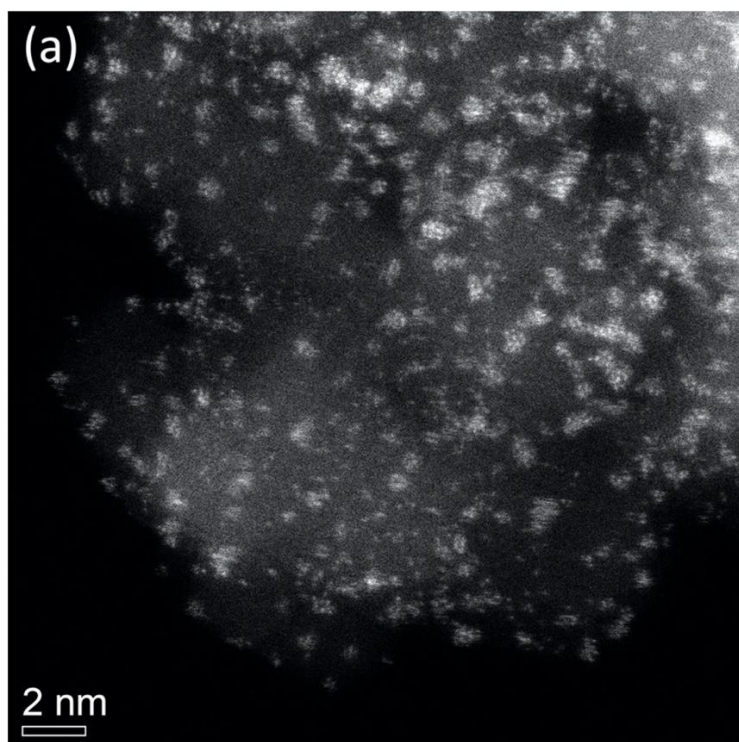


Fig. 7 (a). Distribution of tungsten and rhenium particles (light spots) on the surface of $\alpha$-Al$_2$O$_3$ in the fresh [Re,W]/$\gamma$-Al$_2$O$_3$(K,Ce)/$\alpha$-Al$_2$O$_3$ converter.
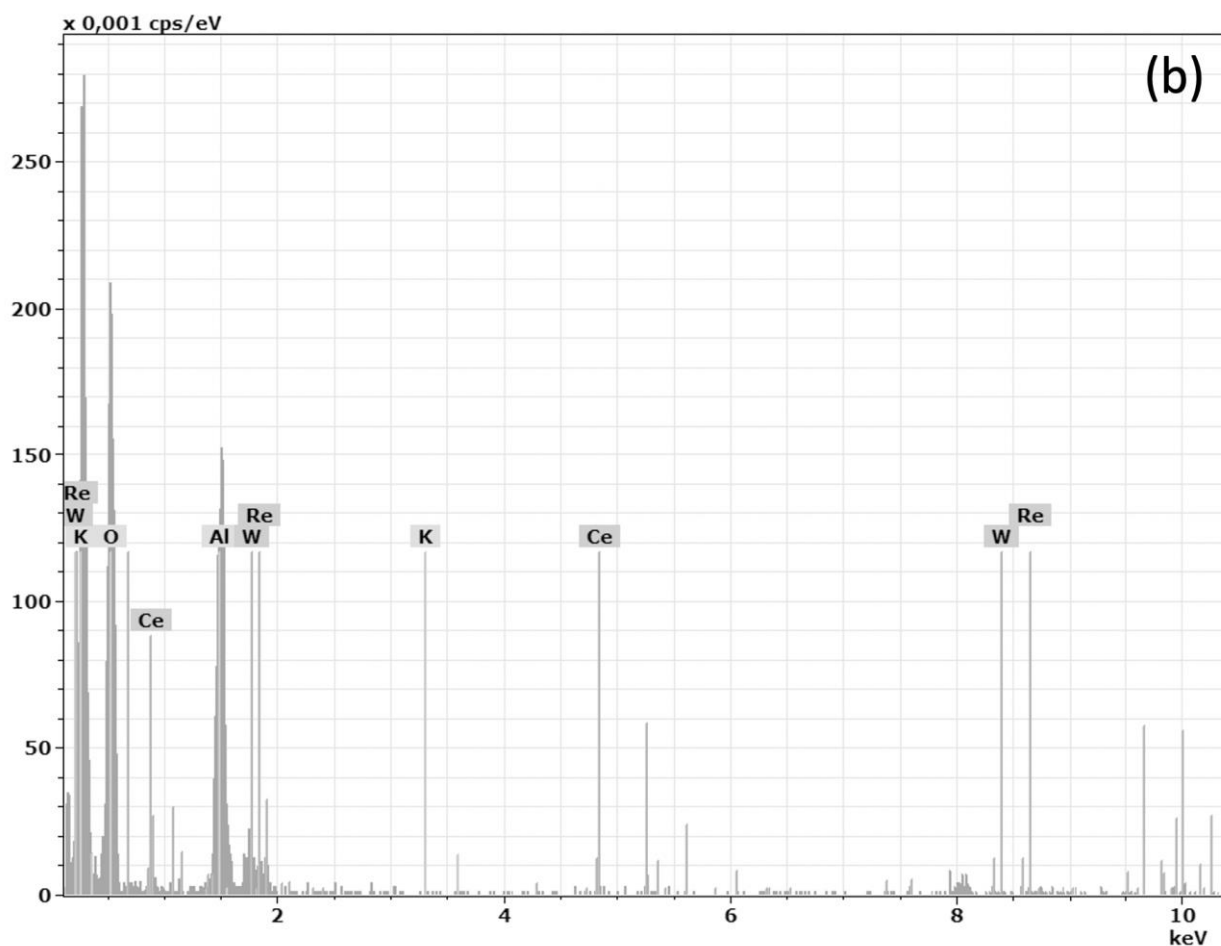
Fig. 7 (b). TEM-EDS-spectrum of distribution of elements on the surface of the fresh [Re,W]/$\gamma$-Al$_2$O$_3$(K,Ce)/$\alpha$-Al$_2$O$_3$ converter.

In turn, on the spent converter, agglomeration of rhenium atoms into nanoclusters is clearly visible, while tungsten particles do not undergo noticeable transformation (Fig. 8 (a, b)). This probably indicates that during dehydrogenation of ethylbenzene rhenium oxides are reduced by the released hydrogen, which leads to the subsequent sintering of the formed metal rhenium particles.

According to the reference data, the deposited tungsten (VI) oxide is reduced at higher temperatures (800 – 900 °C) [29] than those of the dehydrogenation process studied herein, which is probably the reason for the observable stability of fractional composition of tungsten oxide particles.

It is also noteworthy that no traces of carbon deposits were found on the exposed surface of the converter, which is consistent with earlier conclusions about a low degree of coking of the catalyst in the course of dehydrogenation.

Thus, on the basis of the data obtained, it can be assumed that one of the functions of tungsten oxide in the developed system is actually to prevent intensive carbonization of the converter due to the spatial difficulty for the formation of germinal carbon particles on a

catalytically active surface. However, this aspect will be the subject of a more detailed study in a next study.
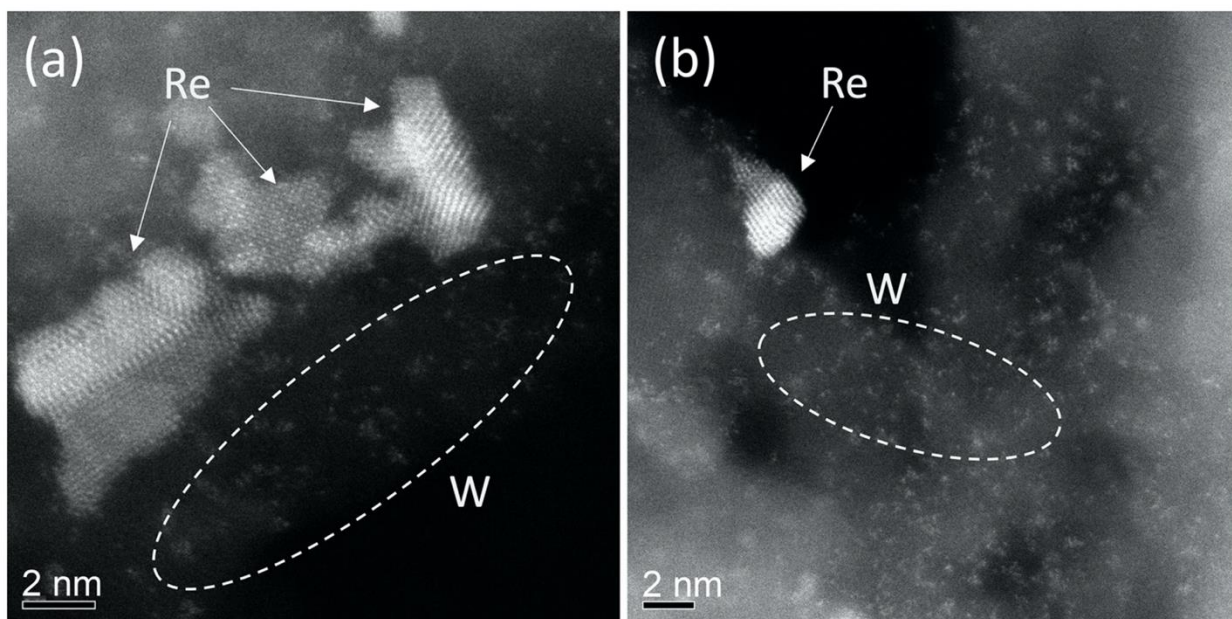


Fig. 8 (a, b) Agglomeration of rhenium particles on the surface of the spent [Re,W]/$\gamma$-Al$_2$O$_3$(K,Ce)/$\alpha$-Al$_2$O$_3$ converter.


Figure 9 shows the XPS spectra on the W 4f and Re 4f energy region at the surface of both fresh and spent converters.

In the fresh and spent samples, a doublet peak corresponding to W 4f core level is present with a W 4f$_{7/2}$ binding energy of 36.1 eV and a doublet separation of 2.1 eV. This is consistent with W$^{6+}$, and the presence of deposited WO$_3$.

As the rhenium Re 4f core levels peaks are overlapping with magnesium Mg 2p photopeaks, it is not possible to determine rhenium oxidation state neither in the fresh sample nor in the spent one.
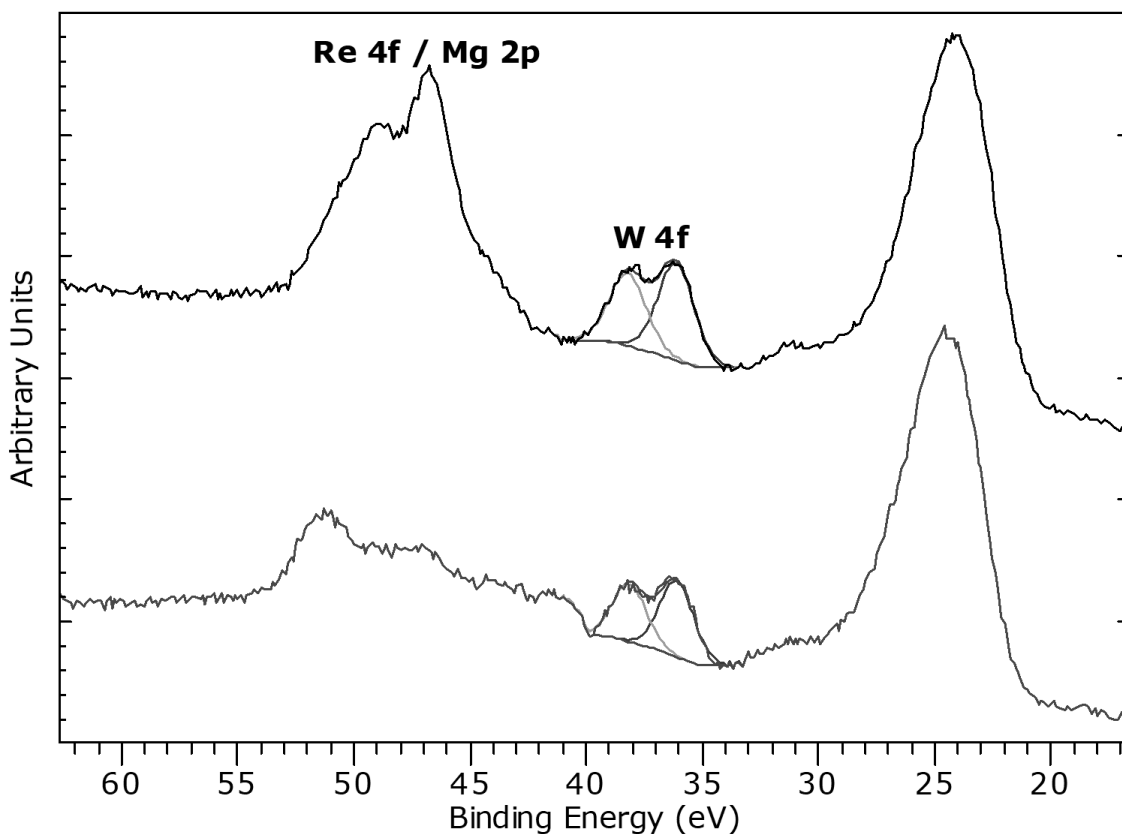
Fig. 9. XPS spectra on the W 4f / Re 4f energy region of the fresh (upper) and spent (lower) [Re,W]/$\gamma$-Al$_2$O$_3$(K,Ce)/$\alpha$-Al$_2$O$_3$ converter.

## Conclusion

We developed a porous ceramic catalytic [Re,W]/$\gamma$-Al$_2$O$_3$(K,Ce)/$\alpha$-Al$_2$O$_3$ converter, obtained through self-propagating high-temperature synthesis and the sol-gel method, for effective dehydrogenation of ethylbenzene to styrene. It was found that on this converter the output of styrene, with a *ca.* 100% selectivity to liquid products, is *approx.* 23 times larger than that on conventional bulk catalysts, while within 6 hours of experiment, the degree of carbonization of the converter does not exceed 5 wt. %

As an advantage of the developed approach over traditional reactors with a bulk catalyst bed, we can stress out improved heat and mass transfers of the reagents in the spatially limited pore volume of the converter, its walls being modified with a small amount of uniformly distributed highly active nanosized catalytic components. This feature is at the base of the observed intensification of the catalytic reaction of dehydrogenation, and the increased resistance of the system to coke formation.

## Acknowledgements

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