

CATALYTIC SYNTHESIS OF DIVINYL FROM ETHANOL

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Abstract

This study investigates the catalytic conversion of ethanol to divinyl under atmospheric pressure and temperatures ranging from 473 to 573 K in a flow-type reactor. Catalysts composed of magnesium, zirconium, and lanthanum oxides supported on SiO₂ were employed. The main products identified during ethanol dehydrogenation were acetaldehyde, methane, and carbon monoxide, alongside minor secondary products such as divinyl, methyl ethyl ketone, butanal, and butanol. The catalytic performance and selectivity were found to depend on both the reaction conditions and the catalyst composition. Mechanistic analysis showed that Lewis acid sites promote aldol condensation of acetaldehyde. IR spectroscopy was used to characterize the active centers of the catalysts, particularly for MgO/SiO₂ and ZrO₂-FeO-ZnO/SiO₂ systems. The results contribute to a better understanding of the reaction pathways and the design of selective catalysts for divinyl production from ethanol.

Keywords: ethanol, catalytic synthesis, divinyl, dehydrogenation, acid-base sites, MgO, ZrO₂, lanthanide oxides.

INTRODUCTION

The production of 1,3-butadiene from ethanol is carried out in two main processes: one-stage (Lebedev process) and two-stage (Ostromyslensky process)[1-2]. Both processes have their own technological advantages and disadvantages. The Lebedev process is a one-stage method, where ethanol is processed in the gas phase and converted directly to butadiene. The main reactions in this process are as follows:

1. Dehydration of ethanol: $C_2H_5OH \rightarrow C_2H_4 + H_2O$
2. Dehydrogenation of ethanol: $C_2H_5OH \rightarrow CH_3CHO + H_2$
3. Condensation of acetaldehyde: $2CH_3CHO \rightarrow CH_2=CH-CH=CH_2 + 2H_2O$

An important aspect of the Lebedev process is that, since it is a one-step process, the process is relatively simple, but the yield of butadiene is lower[3-7].

The Ostromyslensky process is known as a two-stage process. In the first stage, ethanol is converted to acetaldehyde, which is then mixed with ethanol and converted to butadiene in a second reactor:

1. The first step is the dehydrogenation of ethanol:
 $C_2H_5OH \rightarrow CH_3CHO + H_2$
2. Second stage — condensation of acetaldehyde and ethanol mixture: $CH_3CHO + C_2H_5OH \rightarrow CH_2=CH-CH=CH_2 + H_2O$

Catalysts are important in the process of producing butadiene from ethanol. Currently, the most commonly used catalysts are zirconium (ZrO_2), zirconium-silicon (Zr/Si), and calcium-zirconium (CaO/Zr) [8-13].

In the Lebedev process, the single-stage scheme is cheaper because it does not require at least two reactors. However, coke deposition is observed in this process. In the Ostromyslensky process, a high efficiency in butadiene production is achieved by carrying out the process in two stages[14]. The efficiency of the process for producing butadiene from ethanol depends on the type of catalyst and the reaction temperature. Although the single-stage process is distinguished by its simplicity, the two-stage process yields higher butadiene yields.

Materials and methods

A catalytic device for the study of the hydrogenation reaction of ethyl alcohol

The conversion of ethyl alcohol to acetaldehyde was studied in a flow-type catalytic device at a temperature of 473-573 K and atmospheric pressure.

2 g of the catalyst selected for the process, having high catalytic activity and productivity, with a fraction of 0.5-1.0 mm, was placed in a quartz reactor designed for the process, the reactor designed for the process was placed in an oven, its temperature was regulated by a thermostat, and the temperature in the reaction zone was measured by a chromel-alumel thermocouple connected to a digital converter. The reaction products at the outlet of the reactor designed for the process were submitted to chromatographic analysis in the mode of periodic catalyst sampling using a hexagonal screw ring. The reaction product flow line was constantly heated to a temperature of 423 K. Ethyl alcohol was supplied to the reactor designed for the process using a syringe pump. Methane was used as an external standard. All gases were supplied using thermal mass regulators (Brooks). Catalyst sampling was carried out every 30 minutes.

Calculation of indicators of catalytic processes. The selectivity S and the conversion X of ethyl alcohol for the obtained products were calculated using the following formulas:

$$X = \frac{\frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_{\text{ethyl alcohol}} \Omega_{\text{ethyl alcohol}}}{46 \cdot k_{\text{methanol}} \Omega_{\text{methane}}} \cdot 100\%}{\frac{F_{\text{ethyl alcohol}}}{46} - \frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_{\text{ethyl alcohol}} \Omega_{\text{ethyl alcohol}}}{46 \cdot k_{\text{methanol}} \Omega_{\text{methane}}}}$$

$$S_1 = \frac{\frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_t \Omega_t \varepsilon_t}{46 \cdot k_{\text{methanol}} \Omega_{\text{methane}}} \cdot 100\%}{\frac{F_{\text{ethyl alcohol}}}{46} - \frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_{\text{ethyl alcohol}} \Omega_{\text{ethyl alcohol}}}{46 \cdot k_{\text{methanol}} \Omega_{\text{methane}}}} \cdot 100\%$$

$$X = \frac{\frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_{\text{ацетальдегид}} \cdot \Omega_{\text{ацетальдегид}}}{44 \cdot k_{\text{methane}} \cdot \Omega_{\text{methane}}}}{\frac{60 \cdot F_{\text{гелий}} \cdot \frac{p_{\text{ацетальдегид}}}{p}}{R(T + 273,2)} - \frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_{\text{acetaldehyde}} \cdot \Omega_{\text{acetaldehyde}}}{44 \cdot k_{\text{methane}} \cdot \Omega_{\text{methane}}}} \cdot 100\%$$

$$S_1 = \frac{\frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_t \Omega_t \varepsilon_t}{46 \cdot k_{\text{methane}} \Omega_{\text{methane}}} \cdot 100\%}{\frac{F_{\text{ethyl alcohol}}}{46} - \frac{60 \cdot F_{\text{methane}} \cdot p}{R(T + 273,2)} \cdot \frac{16 \cdot k_{\text{acetaldehyde}} \Omega_{\text{acetaldehyde}}}{46 \cdot k_{\text{methanol}} \Omega_{\text{methane}}}} \cdot 100\%$$

Results and discussion

Two types of activated catalytic systems were studied in the dehydrogenation reaction of ethyl alcohol: a) metals supported by silicon oxide b) magnesium, zirconium and lanthanum oxides supported on SiO₂. The characteristics of the catalysts selected for the process, which have high catalytic activity and productivity, are presented in Table 1.

Table 1. Characteristics of catalysts selected for the process with different high catalytic activity and efficiency in the dehydrogenation of ethyl alcohol

A catalyst of choice for process implementation with high catalytic activity and performance	Metal oxide %	Used salt
Cu*FeO*ZnO/SiO ₂	0.90	Cu(NO ₃) ₂ · 3H ₂ O
10 MgO*FeO*ZnO/SiO ₂	11.2	Mg(NO ₃) ₂ · 6H ₂ O
10 La ₂ O ₃ *FeO*ZnO/SiO ₂	10.5	La(NO ₃) ₃ · 6H ₂ O
10 ZrO ₂ *FeO*ZnO/SiO ₂	10.1	ZrO(NO ₃) ₂

All catalysts with high catalytic activity and productivity, selected for the process, were prepared by moisture absorption from solutions of the corresponding precursors until the required concentration was reached. The metal content determined by atomic emission spectroscopy agrees well with the calculated one and allows for a correct comparison of catalysts with high catalytic activity and productivity, selected for the process, from the same group of active components.

The studied catalysts with high catalytic activity and productivity, selected for the implementation of the process, are listed in Table 2.

Table 2. Characteristics of acetaldehyde aldol condensation catalysts

Catalyst	Added metal oxide mass, %	Used salts
5MgO*FeO*ZnO/SiO ₂	5.0	Mg(NO ₃) ₂ · 6H ₂ O
5La ₂ O ₃ *FeO*ZnO/SiO ₂	5.2	La(NO ₃) ₃ · 6H ₂ O
5ZrO ₂ *FeO*ZnO/SiO ₂	5.4	ZrCl ₄
5ZrO ₂ *FeO*ZnO/SiO ₂	5.0	ZrO(NO ₃) ₂ · 2H ₂ O
5Al ₂ O ₃ *FeO*ZnO/SiO ₂	5.2	Al(NO ₃) ₃ · 6H ₂ O

Analytical analysis of the obtained catalysts with high catalytic activity and productivity, selected for the process, showed that the amount of metal oxide in the catalyst samples selected for the production of divinyl from ethyl alcohol with high catalytic properties and productivity, agrees well with the calculated one. For mixed oxides, suitable precursors were first prepared in the form of hydrotalcites with a certain ratio, and then calcined in a nitrogen stream to prevent the formation of Mg carbonates. For comparison, individual magnesium and aluminum oxides obtained using a similar procedure were studied. *Mg/Al*

Similar data on surface area, pore volume, and pore diameter were obtained for the catalysts selected for the process, which had high catalytic activity and productivity, obtained by impregnating silica with appropriate precursors and then calcining.

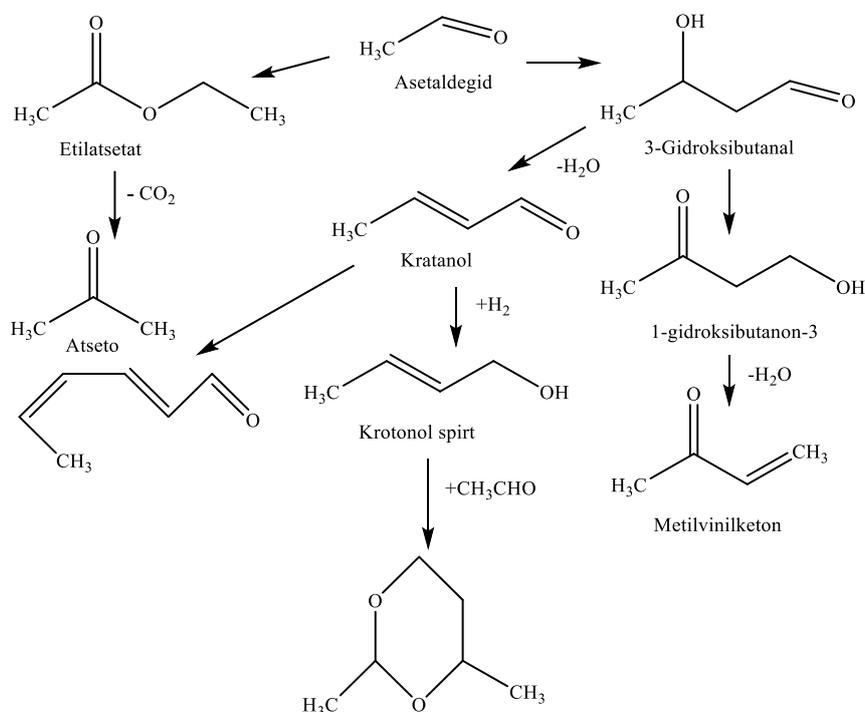
This fact indicates that when using oxides, the carrier holes are not blocked and the



oxide is evenly distributed on the SiO₂ surface.

The mixed oxide catalyst samples selected for the production of divinyl from ethyl alcohol, which has high catalytic properties and yields, and the individual magnesium and aluminum oxides, differ greatly in surface properties and porosity. This is a consequence of the preparation procedure used - no template is used in the synthesis of hydrotalcites, and the porous properties strongly depend on the composition of the solution containing magnesium and aluminum ions, as well as on the composition of the starting materials involved in the reaction used for precipitation.

Ethyl acetate, in turn, can be hydrolyzed to produce ethyl alcohol and acetic acid, which are decarboxylated to acetone. Aldol condensation of acetaldehyde with crotonaldehyde gives 2,4-hexadienal. Reduction of crotonaldehyde to 1-hydroxy-2-butylene followed by Prins reaction with acetaldehyde gives 2,4-dimethyl-1,3-dioxane:



Catalytic properties of catalyst samples selected for the production of divinyl from ethyl alcohol with high catalytic activity and productivity. To compare the activity of catalysts selected for the process with high catalytic activity and productivity, the initial rates of acetaldehyde conversion and crotonaldehyde formation were experimentally determined in the range of acetaldehyde conversion from 0 to 15%.

The catalysts selected for the process, which have high catalytic activity and productivity, showed high activity and selectivity. For most of the main catalysts selected for the process, which have high catalytic activity and productivity, the initial rate of crotonaldehyde formation is higher than 100 μmol / g-s, and the selectivity for crotonaldehyde is more than 70%. However, these catalysts, which have high catalytic activity and productivity, were deactivated within 2 hours due to the poisoning of the active sites by heavy by-products. To study the aldol condensation reaction of acetaldehyde in acidic and basic

systems in more detail and to determine the type of active sites required for the selective occurrence of the reaction, we selected two model catalytic systems based on silicon-based magnesium and zirconium oxides.

Study of the mechanism of aldol condensation of acetaldehyde in acidic and basic catalytic systems. To study the mechanism of the aldol condensation of acetaldehyde, $2\text{MgO}/\text{SiO}_2$ and $2\text{ZrO}_2*\text{FeO}*\text{ZnO}/\text{SiO}_2$ catalysts with a mass fraction of MgO and ZrO_2 of 2% were prepared, which had high catalytic activity and productivity and were selected for the process.

Physico-chemical properties of model systems. The surface ON groups of the model catalysts with high catalytic activity and productivity, selected for the process implementation, were studied by IR spectroscopy.

The IR spectrum of native silica contains a hot band at 3745 cm^{-1} , which is associated with isolated Si-OH groups. The addition of MgO and ZrO_2 oxides leads to a significant decrease in the intensity of this peak and its broadening towards the lower frequency range. This result may be due to the strong oxide-activator interaction with the formation of mixed oxides ($=\text{Si-OM}=\text{}$) on the support surface.

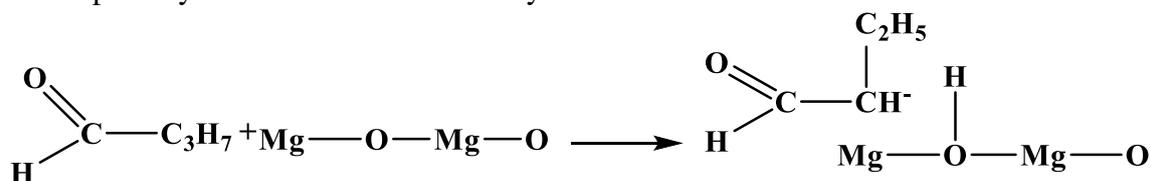
The main properties of the catalysts selected for the model, which have high catalytic activity and productivity, were studied by the TPD- CO_2 method. The TPD- CO_2 curves for the catalyst samples $2\text{ZrO}_2*\text{FeO}*\text{ZnO}/\text{SiO}_2$ and SiO_2 , which have high catalytic activity and productivity, selected for the production of divinyl from ethyl alcohol, are practically the same, except for a high temperature peak at 700 K for $2\text{ZrO}_2*\text{FeO}*\text{ZnO}/\text{SiO}_2$. For the catalyst selected for the process $2\text{MgO}/\text{SiO}_2$, which has high catalytic activity and productivity, a strong peak is observed at 373 K, which corresponds to the desorption of CO_2 from weak basic centers. These data are in good agreement with the literature data. The main properties of activated oxides differ significantly from those of common MgO and ZrO_2 due to the high dispersion of SiO_2 activated oxides. This is due to the number of key centers on the surface of the catalyst selected for the process, which have high catalytic activity and productivity.

For the $2\text{MgO}/\text{SiO}_2$ system, intense lines corresponding to CO_2 adsorption at the main centers are observed in the $1450\text{-}1700\text{ cm}^{-1}$ wavenumber region, while for the $2\text{ZrO}_2*\text{FeO}*\text{ZnO}/\text{SiO}_2$ catalyst samples, the intensity of these lines is much lower. According to the literature, these bands can be associated with vibrations of three types of surface species: bicarbonate, mono- and bidentate carbonate. According to the literature, these bands can be associated with vibrations of three types of surface species: bicarbonate, mono- and bidentate carbonate. The bands at 1709 and 1492 cm^{-1} represent the nonsymmetric and asymmetric vibrations of the $\text{O}=\text{C}=\text{O}$ bond in bicarbonate, which are formed as a result of interaction with weak basic OH groups on the $2\text{MgO}/\text{SiO}_2$ surface and are easily destroyed upon pumping at 373 K. The band at 1673 cm^{-1} can be associated with vibrations of bidentate carbonate species formed on the surface of Lewis acid-base ion pairs. The bands at 1610 and 1450 cm^{-1} can be associated with monodentate carbonate species formed during the adsorption of CO_2 on isolated O_2^- centers. Thus, the $2\text{MgO}/\text{SiO}_2$ catalyst, which has high catalytic activity and productivity, selected for the process, has three types of basic centers on its surface: strong basic centers represented mainly by isolated O_2^- ions, medium-strength centers represented by Lewis acid-base pairs bound by Mg-O particles, and silica and weak basic OH groups.

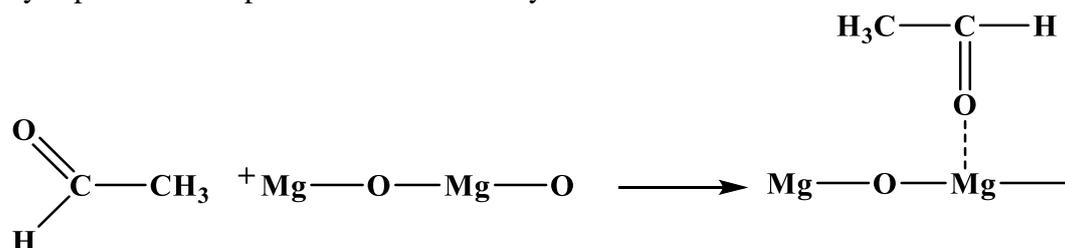
In contrast to the original SiO_2 , the appearance of new lines at 1608, 1491 and 1446 cm^{-1} is observed for the catalysts selected for the process, which have high catalytic activity

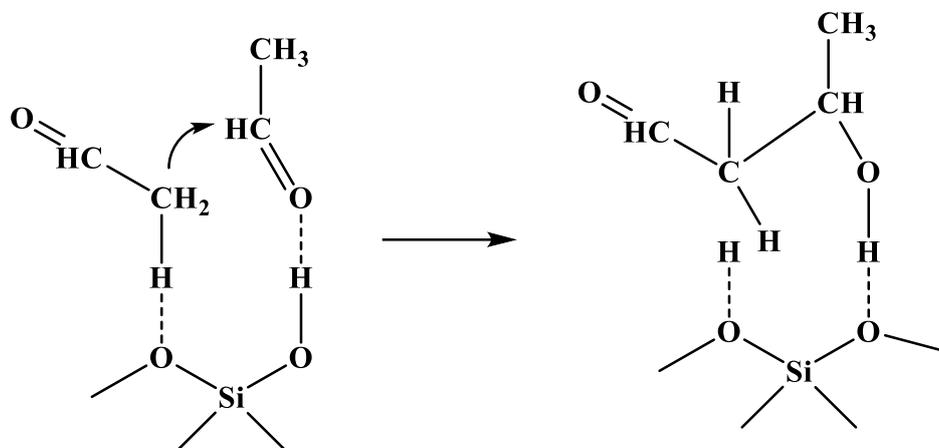
and productivity, $2\text{MgO}/\text{SiO}_2$ and $2\text{ZrO}_2 \cdot \text{FeO} \cdot \text{ZnO}/\text{SiO}_2$. These lines can be associated with the adsorption of pyridine at Lewis acid centers. The appearance of Lewis acid for activated zirconium oxide can be associated with the dehydroxylation of ZrO_2 after calcination. In $2\text{MgO}/\text{SiO}_2$, the Lewis acidity can be manifested by the coordinatively unsaturated Mg cations on the faces and edges of MgO crystallites. For the catalysts $2\text{MgO}/\text{SiO}_2$ and $2\text{ZrO}_2 \cdot \text{FeO} \cdot \text{ZnO}/\text{SiO}_2$, which have high catalytic activity and yield, the selectivity for crotonaldehyde is slightly higher than for the $5\text{MgO}/\text{SiO}_2$ and $5\text{ZrO}_2 \cdot \text{FeO} \cdot \text{ZnO}/\text{SiO}_2$ systems (88 and 83%, respectively), which is associated with a decrease in the yield of the aldol condensation reactions. However, crotonaldehyde and acetaldehyde lead to the formation of heavy products. The method of selective poisoning of active centers was used to study the nature of the centers necessary for the aldol condensation reaction of acetaldehyde. We used carbonic anhydride as a molecular probe for the main centers, and pyridine was used to poison the acid centers. Under experimental conditions, these substances do not interact with acetaldehyde and do not affect the composition of the formed products. The initial rate of croton aldehyde formation was determined experimentally to compare the activity of catalysts selected for the process, which have high catalytic activity and productivity in the presence and absence of probe molecules.

The addition of CO_2 to the reaction mass does not lead to a change in the activity of the catalysts selected for the process, which have high catalytic activity and productivity, unlike pyridine, which leads to a significant slowdown of the reaction for both catalysts, which have high catalytic activity and productivity, which have been selected for the process. The significant decrease in the activity of the catalysts selected for the process, which have high catalytic activity and productivity, with the addition of pyridine indicates that Lewis acid centers play an important role in the aldol condensation of acetaldehyde at acidic and basic centers. CO_2 adsorption led to a significant decrease in activity, while ammonia adsorption did not affect the activity. This fact can be explained by the different activation mechanisms of acetaldehyde and butyral. The removal of a proton from the secondary carbon atom of butyral should occur more easily at the main centers of magnesium oxide than the removal of a proton from the primary carbon atom of acetaldehyde:



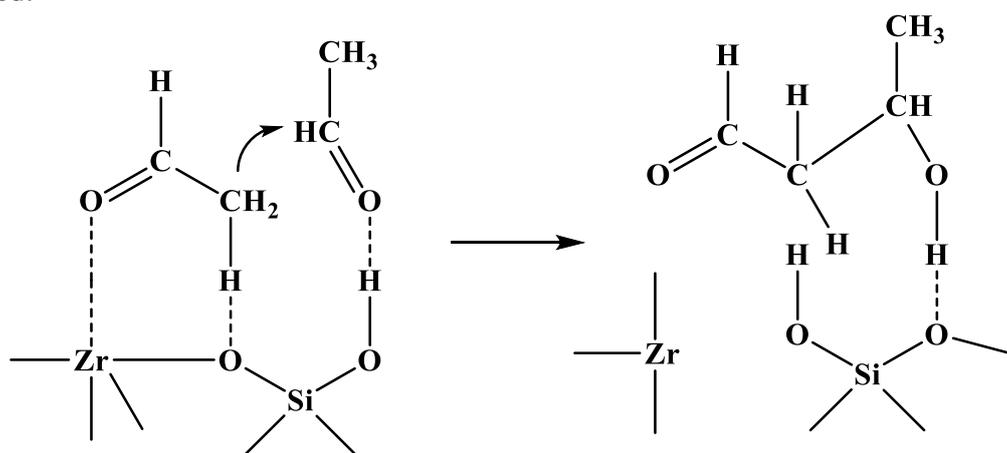
It can be assumed that the activation of acetaldehyde at Lewis acidic centers leads to the easy separation of a proton from acetaldehyde:





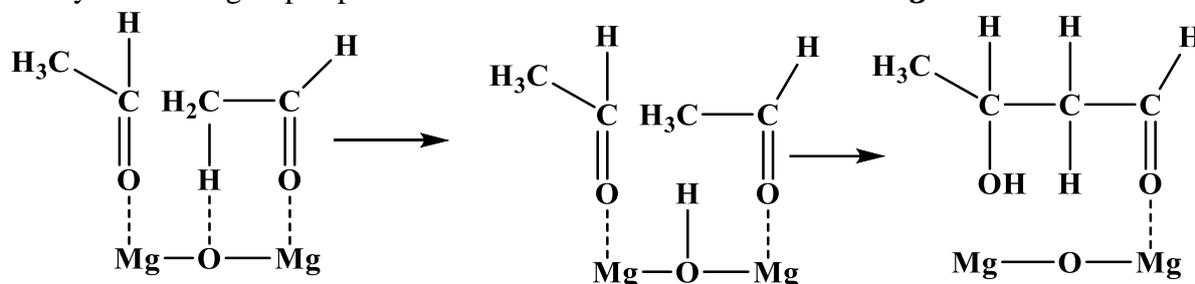
Further increase in temperature does not lead to a change in the spectra.

To study the role of acidic and basic centers in the condensation reaction of acetaldehyde to crotonaldehyde, the reaction was carried out with CO₂ and pyridine pre-adsorbed on them on catalysts with high catalytic activity and yield, selected for the process, which have high catalytic properties and yield, on catalyst samples selected for the production of divinyl from ethyl alcohol. The initial adsorption of carbonic anhydride does not lead to a change in the intensity and position of the adsorbed acetaldehyde peaks, while the adsorption of pyridine leads to a significant decrease in the intensity of the lines and inhibition of the crotonaldehyde formation reaction over the entire temperature range. As a result, the initial adsorption of pyridine leads to a weakening of the binding of acetaldehyde to the surface and stops the aldolization process. Thus, the obtained spectral data confirm the hypothesis of the participation of Lewis acid centers and surface groups in the reaction and show an increase in the activity of 2ZrO₂*FeO*ZnO/SiO₂ relative to SiO₂. Based on the obtained data, the following mechanism of aldol condensation of acetaldehyde on 2ZrO₂*FeO*ZnO/SiO₂ can be proposed.



According to this mechanism, the introduction of zirconium oxide into silica leads to the formation of Lewis acid centers and an increase in the Brønsted acidity of silanol groups. The catalyst selected for the process, 2ZrO₂*FeO*ZnO/SiO₂, which has high catalytic activity and productivity, is almost completely converted to acetaldehyde at 373K, while the catalyst selected for the process, 2MgO/SiO₂, which has high catalytic activity and productivity, is not completely converted even at 453K.

Strong interaction of acetaldehyde with Si-OH may be the result of the induction of acidity of silanol groups upon interaction of the centers with CO₂: $-Mg - O - Si - OH$

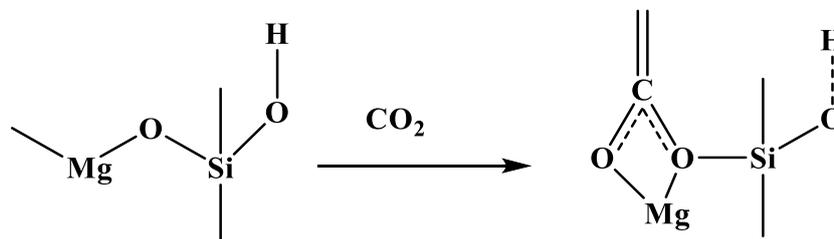


The results obtained show that the strong basic centers located on the surface of the 2MgO/SiO₂ catalyst, which has high catalytic activity and productivity, are more active than the Lewis centers of the 2ZrO₂*FeO*ZnO/SiO₂ catalyst, which has high catalytic activity and productivity, and is selected for the process.

However, they are quickly quenched and then the reaction proceeds in the form of a "Lewis center - weak base" ion pair, similar to the mechanism described for 2ZrO₂*FeO*ZnO/SiO₂. To verify this, experiments on the initial adsorption of pyridine on 2MgO/SiO₂ catalyst samples were carried out (Fig. 6.10). As in the case of 2ZrO₂*FeO*ZnO/SiO₂, the initial adsorption of pyridine leads to the almost complete disappearance of the peaks corresponding to the bond vibrations in acetaldehyde and crotonaldehyde, which indicates the participation of Lewis acid centers in the condensation reaction of acetaldehyde. Thus, studies using IR spectroscopy show that the aldol condensation reaction of acetaldehyde can proceed by two mechanisms on the 2MgO/SiO₂ catalyst chosen for the process, which has high catalytic activity and productivity:

- basic mechanism, including carbanion formation at strong basic centers and
- Synchronous mechanism involving activation in "Lewis center - weak base" pairs.

The synchronous mechanism is likely to occur under the reaction conditions of the flow reactor designed for the process on the 2ZrO₂*FeO*ZnO/SiO₂ and 2MgO/SiO₂ catalysts with high catalytic activity and productivity, which is in good agreement with the data on the selective poisoning of the catalysts with high catalytic activity and productivity by the addition of probe molecules.



CONCLUSION

In this study, the dehydrogenation reaction of ethyl alcohol was studied in a flow-type catalytic device at a temperature of 473-573 K and atmospheric pressure. Metals supported by silicon oxide and magnesium, zirconium and lanthanum oxides activated on SiO₂ were used as the catalytic system. Based on the results of the study, it was determined that acetaldehyde, methane and carbon monoxide are the main products in the dehydrogenation process of ethyl alcohol. The activity and selectivity of the catalysts were confirmed to be very high. The main product in the reaction is acetaldehyde, and in the high conversion region, methyl ethyl ketone

and ethyl acetate are formed as secondary products. The role of the active centers of the catalysts in the reaction and their mechanism of action were determined. It was shown that the mechanism of aldol condensation of acetaldehyde in catalytic systems consisting of acidic and basic centers is associated with Lewis acid centers. Also, the surface properties and porosity of the $2\text{MgO}/\text{SiO}_2$ and $2\text{ZrO}_2*\text{FeO}*\text{ZnO}/\text{SiO}_2$ model catalytic systems were analyzed. The results obtained during the study are of great importance in diagnosing the activity and assessing the selectivity of catalytic systems in the production of acetaldehyde from ethyl alcohol. It was found that the high catalytic activity of the catalysts is associated with the properties of their surface properties and active centers.

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