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STUDY OF ACTIVE CENTERS OF CROTON ALDEHYDE REDUCTION REACTION

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It is very desirable to have information about the nature and structure of the active centers in order to create a catalyst of choice for the process, which has high catalytic activity and productivity for the conversion of ethyl alcohol to divinyl. Calculations have shown that the reaction mechanism includes the following steps:

1) Adsorption of alcohol and ketone on Lewis acid centers;

2) deprotonation of alcohol to form alkoxide;

3) hydride transfer from the alkoxide to the carbonyl group of the ketone through a 6-membered transition state. Partially hydrolyzed Lewis acid centers have been proposed as active centers.

In this work, an attempt was made to find a correlation between the total number of acid centers detected by ammonia TPD and the catalytic activity and relative number of Lewis acids of various Zr-containing catalysts selected for the reduction of crotonaldehyde with ethyl alcohol, which had high catalytic activity and productivity. The surface OH groups were determined by IR spectroscopy of adsorbed CO. The results show that the catalytic activity does not depend on either the total number of acid centers or the number of surface OH groups. On the contrary, a good correlation was found with the number of Lewis acid centers of zirconium. The initial rate of formation of 1-hydroxy-2-butylene and the relative amount of Zr4+ Lewis acid centers increase in a series of catalysts selected for the process, which have the same high catalytic activity and yield: Zr-HSZ < ZrO_2*FeO*ZnO/SiO_2 < ZrO_2. The catalyst samples selected for the production of divinyl from ethyl alcohol, ZrO_2/ZrO_2 and ZrO_2/La_2O_3, which do not have Lewis Zr4+ centers, are completely inactive in the reaction. Thus, our results indicate that the Lewis centers of Zr^{4+} play a major role in the MPVO reaction. In order to

determine the type of centers responsible for the formation of ethoxide particles, experiments were conducted to study the initial stages of the reaction on Zr-HSZ catalyst samples using IR spectroscopy. Deuteroethanol C_2H_5OD, dried with molecular sieve 3A, was used to distinguish the OH groups of the catalyst and substrate, which had high catalytic activity and productivity, selected for the process. C_2H_5OD was injected into the IR in small portions, and after equilibrium was established, the spectra of surface compounds were recorded.

When the mass fraction of acetaldehyde increases from 4 to 15%, no significant change in the selectivity for divinyl is observed, while the yield of divinyl increases from 9 to 28% (Fig. 2, Table 3). A further increase in the amount of acetaldehyde in the feedstock leads to a significant decrease in the selectivity for divinyl, and the selectivity for heavy adducts containing C6+ increases. This fact indicates that at high acetaldehyde concentrations, the yield of the aldol condensation increases, leading to a decrease in the selectivity of the entire process. The curve of the total conversion of acetaldehyde and ethyl alcohol passes through a maximum, which fits well with the reaction scheme, and the reduction of crotonaldehyde to 1-hydroxy-2-butylene requires a reducing agent, and the decrease in the content of ethyl alcohol leads to a decrease in the catalyst selected for the process, which has high catalytic activity and productivity.

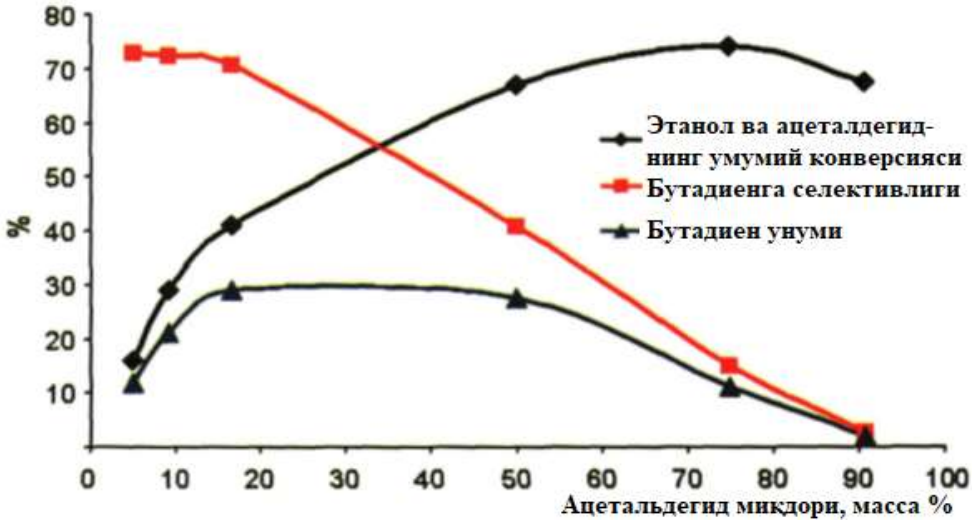

Figure 2. Dependence of raw material and selectivity of divinyl conversion on raw material composition (mass rate of raw material 0.3 g/g h, T = 593K)

Effect of type of metal. In the first stage, the effect of the methyl nature responsible for the hydrogenation of ethyl alcohol to acetaldehyde on the efficiency

of the process was studied. For this purpose, catalyst samples selected for the production of divinyl from ethyl alcohol with high catalytic properties and productivity based on ZrO_2*FeO*ZnO/SiO_2 with various metals (Zr, La, Cu, Ni) were prepared and tested in the synthesis reaction of divinyl from ethyl alcohol. The results are presented in Table 3. The catalyst samples selected for the production of divinyl from ethyl alcohol with high catalytic properties and productivity based on copper and silver showed similar conversion and selectivity for divinyl (~ 74%). The catalyst selected for the process with high catalytic activity and productivity containing Zr has a slightly lower selectivity for divinyl (66%) due to the formation of butylenes.

Table 3. Effect of metal type in divinyl synthesis reaction (mass rate of raw material 0.3 g/g-h, T = 600K, reaction time 300 min)

	0.3La/4ZrO_2*FeO*ZnO/SiO_2	0.3Ni/4ZrO_2*FeO*ZnO/SiO_2	0.3Cu/4ZrO_2*FeO*ZnO/SiO_2
Conversion of ethyl alcohol to acetaldehyde,%	30.0	26.8	10.3
Product selectivity, %			
Divinyl	73.8	73.5	67.9
Ethylene	2.7	2.6	5.8
Propylene	3.0	3.7	3.7
Butylenes	2.9	3.6	5.7
Diethyl ether	3.7	3.3	6.4
Ethyl acetate	1.6	1.6	2.7
Butanol-1	3.0	3.4	2.6
Heavy products	9.3	8.4	5.3

To study the deactivation of catalysts with high catalytic activity and productivity, the dependence of the divinyl yield per unit mass of catalyst with high catalytic activity and productivity on the reaction time was analyzed (Fig. 3). The

catalyst with high catalytic activity and productivity, containing Ni, showed good stability - the divinyl yield did not change almost during the 9-hour experiment. On the contrary, the catalysts with high catalytic activity and productivity, containing lanthanum and copper, were passivated. The fact that nickel can resist the deactivation of the catalyst with high catalytic activity and productivity, which is explained by the cleavage of coke precursors on the surface of the catalyst with high catalytic activity and productivity, is explained by the formation of coke precursors on the surface of the catalyst with high catalytic activity and productivity. Among the catalysts selected for the process, which have high catalytic activity and productivity, containing Cu and Ag, $0.3La/4ZrO_2/SiO_2$ showed high stability over time. It should also be noted that the selectivity towards the target product and by-products did not change during the experiment, which may indicate that the reaction mechanism does not change with the gradual poisoning of the active sites.

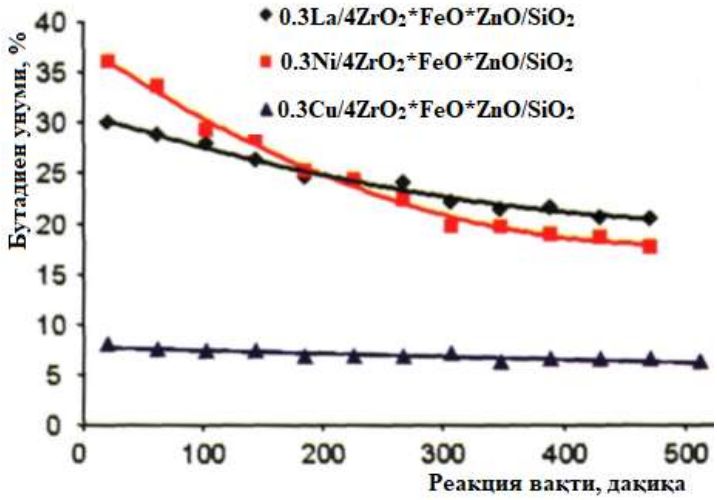

Figure 3. Dependence of divinyl yield on reaction time with various metals with catalysts having high catalytic activity and productivity, selected for the process (mass feed of raw material 0.3 g/g-h, T = 593 K).

Based on experimental data on the selectivity and stability of the target divinyl over time, a catalyst with high catalytic activity and productivity, including zirconium, was selected for further studies to carry out the process.

Effect of oxide type. In subsequent experiments, catalysts with high catalytic activity and productivity of various oxides were synthesized and studied. The catalyst with high catalytic activity and productivity of the selected catalyst samples for the production of divinyl from ethyl alcohol with high catalytic properties and

productivity were compared at the same ethyl alcohol conversion, which was achieved by changing the mass flow rate of the feedstock. The catalytic activity of the catalyst with high catalytic activity and productivity of the selected catalyst for the process can be attributed to such a high concentration of acid centers, as well as the presence of Brønsted acid centers on the surface, which are active in the dehydration reaction. High yields of heavy products (up to 27%) were observed on the catalysts with high catalytic activity and productivity of ZrO_2 and MgO. This result indicates that magnesium and zirconium oxides are very active in the aldol condensation reaction, and it seems that the crotonaldehyde formed in the first step reacts with the subsequent acetaldehyde molecule to form unsaturated alcohols with carbonyl compounds at C^{6+}. The reduction of the latter leads to the formation of dehydrating hexatrienes and their derivatives.

The highest selectivity for divinyl was demonstrated by the catalysts $0.3La/4ZrO_2*FeO*ZnO/SiO_2$ (74%) and 0.3La/Zr-HSZ (62%) with high catalytic activity and yield, which were selected for the process, containing Zr-containing components responsible for the aldol condensation and reduction of crotonaldehyde. The catalyst Zr-HSZ with high catalytic activity and yield, which was selected for the process, showed high resistance to deactivation during the first 4 hours of operation, but over time, the deactivation rate increased significantly due to the blocking of the pores of the mesoporous zeolite with high sorption and catalytic properties by compaction products. Other catalysts with high catalytic activity and productivity, selected for the process, had similar productivity over time. The maximum productivity of divinyl was observed at $0.3Zr/4ZrO_2*FeO*ZnO/SiO_2$.

Table 4. Effect of zirconium oxide content on the main parameters of divinyl synthesis reaction (mass consumption of raw materials 0.3 g/g-hour, T = 593K, reaction time 300 min)

	$Zr/4ZrO_2*FeO*ZnO/SiO_2$	$Zr/10ZrO_2*FeO*ZnO/SiO_2$	$Zr/18ZrO_2*FeO*ZnO/SiO_2$
Conversion of ethyl alcohol to acetaldehyde,%	48.0	45.6	45.8
Product selectivity, %			
Divinyl	72.1	73.0	72.8
Ethylene	1.5	2.1	2.3
Propylene	3.0	2.9	2.9

Butylenes	2.9	2.6	2.5
Diethyl ether	3.1	2.4	3.0
Ethyl acetate	3.0	2.9	3.0
Butanol-1	1.7	2.5	2.8
Heavy products	12.7	11.7	10.8

During the experiments, all the studied catalysts with high catalytic activity and productivity, selected for the process, were deactivated. At the same time, the deactivation rate changed slightly: with increasing ZrO_2 content, a slight decrease in the deactivation rate was observed, as indicated by a change in the slope of the divinyl productivity curve over time. This dependence indicates that the deactivation of the catalysts with high catalytic activity and productivity, selected for the process, may be associated with poisoning of the active centers of zirconium oxide.

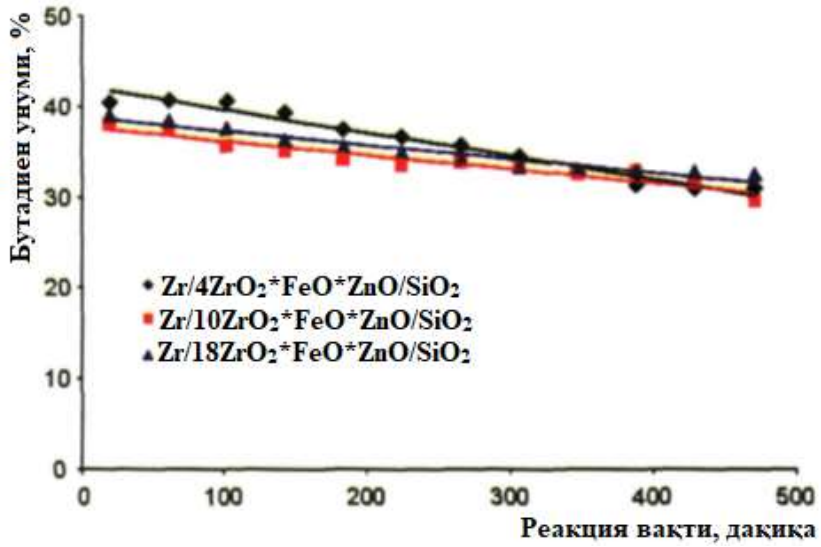

Figure 4. Dependence of divinyl yield on reaction time on catalysts with high catalytic activity and productivity containing zirconium oxide with different compositions (mass rate of raw material 0.3 g/g-h, T = 593 K).

References

1. Licht F.O. World ethanol production to rebound in 2021. Available from: https://informaconnect.com/world-ethanolproduction-to-rebound-in-2021/ (accessed October 2022).
2. Dussol D., Cadran N., Laloue N., Renaudot L., Schweitzer J.M. Chem. Eng. J. – 2020. – Vol. 391. – Article no. 123586.
3. Angelici C., Velthoen M.E.Z., Weckhuysen B.M., Bruijnincx P.C.A. ChemSusChem. – 2014. – Vol. 7. – P. 2505–2515.
4. Ochoa J.V., Bandinelli C., Vozniuk O., Chieregato A., Malmusi A., Recchia C., Cavani F. Green Chem. – 2016. – Vol. 18. – P. 1653–1663.
5. Shylesh S., Gokhale A.A., Scown C.D., Kim D., Ho C.R., Bell A.T. ChemSusChem. – 2016. – Vol. 9. – P. 1462–1472.