

Isopropanol conversion over binary titan vanadium oxide catalysts

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Abstract: Isopropanol conversion over binary titan vanadium oxide catalysts in the presence and absence of oxygen were studied. It was shown that acetone and propylene are the main products of the isopropanol dehydrogenation reaction over studied catalysts. It is established that in the isopropanol dehydrogenation reaction over titanium-vanadium oxide catalysts, the samples with an equimolar ratio of initial elements are highly active. In the dehydrogenation reaction of isopropyl alcohol in the presence of oxygen, except for the catalyst Ti-V=1-9, all other binary titanium-vanadium oxide catalysts have high activity in the propylene formation reaction. It was found that on binary titan-vanadium oxide catalysts in the isopropanol dehydrogenation reaction in the absence of oxygen, the increase in surface acidity leads to an enhancement in acetone yield and a lowering in propylene yield. In the isopropanol dehydrogenation reaction in the presence of oxygen, the change of surface acidity does not lead to a change in the yields of reaction products.

Keywords: Isopropanol; Dehydrogenation; Oxidative dehydrogenation; Vanadium oxide; Isomerization.

1. Introduction

In recent years, in connection with the transition to the use of environmentally friendly technologies and the decrease in the negative environmental impact of industry, there has been an increase in interest in the use of renewable raw materials in the chemical industry, such as ethanol, isopropanol, butanol¹⁻³. Isopropanol is one of the important renewable chemicals for the chemical industry. For example, it produces acetone, ethers and esters, fuels, etc.⁴⁻⁶. Often, isopropyl alcohol is also used as a solvent for catalytic reactions in the liquid phase⁷.

Various catalytic systems have been proposed for isopropyl alcohol conversion reactions. The study of the effect of Li₂O doping on the surface and catalytic properties of the NiO/MgO system has shown that the activity of catalysts in dehydrogenating isopropanol into acetone increases with increasing dopant content⁸. The doping process does not change the activation energy of the catalyzed reaction but instead changes the concentration of catalytically active components without changing their nature of energy. A study of the activity of Rh catalysts deposited on CeO₂, Al₂O₃, SiO₂, ZrO₂, MgO, or TiO₂ in the reaction of steam reforming of 2-propanol showed that their activity depended significantly on the type of carrier⁹. The CeO₂-based catalyst had the highest selectivity, probably because it had the longest extended lifetime. The reaction kinetics of the interaction of isopropyl alcohol with

acetic acid to produce isopropyl acetate and water was studied on a solid resin catalyst¹⁰. A pseudohomogeneous kinetic model was proposed based on the results obtained, and the reaction rate constants and activation energies were calculated. Oxides of such elements as titanium and vanadium are widely used in oxidation reactions of low molecular weight alcohols, particularly in the oxidation of isopropyl alcohol^{11,12}.

Previously, we have shown that isopropanol on binary vanadium-containing catalysts is converted rapidly into products such as propylene and acetone^{13,14}. One of the main properties of solid catalysts that impact their activity is the acidic properties of their surface¹⁵⁻¹⁷. In order to characterize the acid-base properties of the surface under conditions approximating natural catalytic reactions, some catalytic reactions are widely used as model reactions^{18,19}. Reactions such as dehydration of propanol-2, butanol-2, isomerization of olefins, etc., are used for this purpose^{20,21}. To characterize the acidic properties of the surface of binary Ti-V-O catalysts under conditions close to catalysis, we used the conversion of butene-1 into trans and cis butenes-2, which is convenient due to its simplicity^{22,23}. According to literature data, the total yield of trans and cis butenes-2 in the isomerization reaction correlates well with the total surface acidity determined by potentiometric titration and other methods²⁴. Therefore, in this paper, we studied the

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effect of the composition and the catalyst surface acidity on the activity of binary Ti-V-O catalysts in the reactions of dehydrogenation of isopropyl alcohol in the presence and absence of oxygen.

2. Experimental

Binary titanium-vanadium oxide catalysts of various compositions were prepared by co-precipitation from aqueous titanium tetrachloride and ammonium metavanadate solutions. The resulting mixtures were evaporated at 95-100°C, then the precipitates formed were dried at 100-120°C and then decomposed until nitrogen oxides and chlorine were completely emitted at about 250°C. The obtained solid masses were calcined at a temperature of 700°C for 10 hours. In this way, we have prepared 9 catalysts with an atomic ratio of initial elements from Ti: V=1:9 to Ti: V=9:1.

The activity of titanium-vanadium oxide catalysts was studied in a flow unit with a tubular reactor in the temperature range of 150-450°C every 50°C. In the oxidation of isopropyl alcohol, the ratio of initial reagents isopropyl alcohol: air: nitrogen was 1:2:8. Conversion of isopropyl alcohol in the absence of oxygen was carried out at the ratio of initial reagents isopropyl alcohol: nitrogen = 1:10. The volumetric feed rate of the feedstock was 1200 h⁻¹. 5 ml of the investigated catalyst with a grain size of 1.0-2.0 mm was loaded into a quartz reactor and its activity in the oxidation reaction of isopropyl alcohol was studied. The yields of isopropyl alcohol conversion products, as well as the amount of unreacted alcohol, were determined on a chromatograph with a flame ionization detector and a 2-m column filled with a

specially treated Polysorb-1 sorbent. The carbon dioxide formed was determined on a chromatograph with a 6-meter column filled with a Celite sorbent coated with vaseline oil.

3. Results and Discussion

The research of the catalytic activity of the studied catalysts showed us that the main products of the isopropyl alcohol dehydrogenation reaction in the absence of oxygen on the Ti-V-O catalytic system are acetone, propylene and, at high temperatures, an insignificant amount of carbon dioxide and decomposition products. As example, the dependence of the activity of the Ti-V=7-3 catalyst in the isopropyl alcohol conversion reaction on temperature is given in Figure 1. It can be seen that the isopropyl alcohol conversion reaction over this catalyst starts at 200°C with the formation of 3.4% acetone and 30.4% propylene. As the reaction temperature increases, the outputs of propylene and acetone pass through a maximum of 300°C and 250°C, respectively. At these temperatures, the highest yields of acetone and propylene, 18.7% and 55.5%, respectively, are observed. In addition to acetone and propylene, carbon dioxide formation is observed in the studied sample starting from 350°C. The output of carbon dioxide increases with the rising of the reaction temperature over the whole temperature range investigated. The maximum yield of carbon dioxide is observed at 400°C equal to 2.7%. Figure 1 shows that the maximal isopropanol conversion on the Ti-V=7-3 catalyst at 400°C is 73.8%.

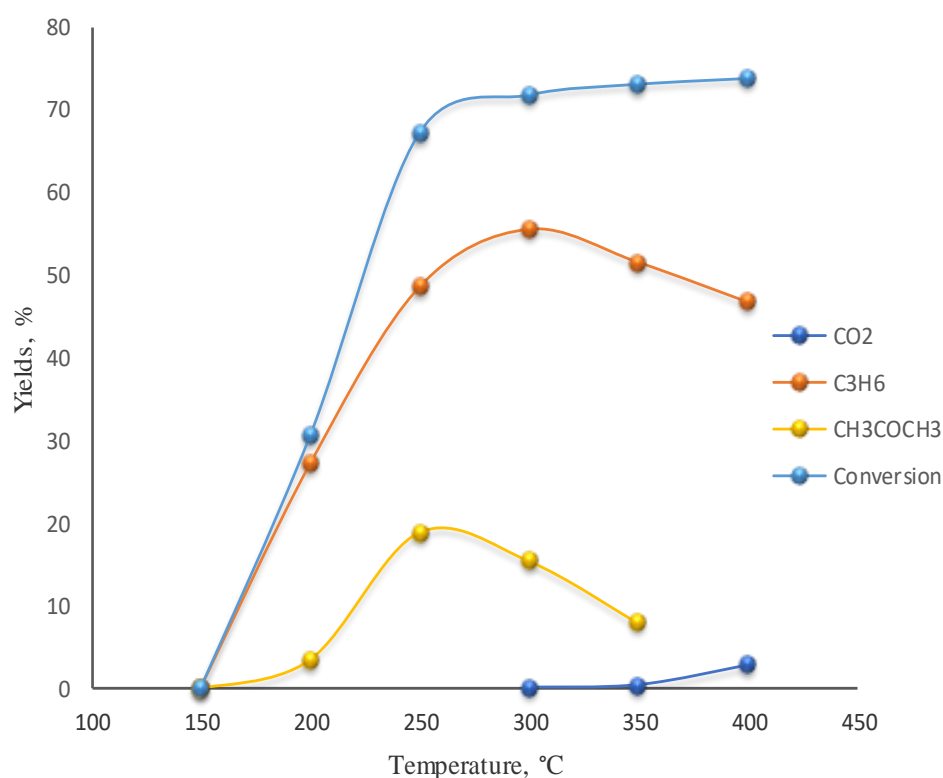


Figure 1. Temperature affects the yields of isopropanol dehydrogenation reaction products on catalyst Ti- V=7-3

We also studied the influence of catalyst composition on their activity in the reaction of isopropanol conversion without oxygen. Figure 2 shows the results of the effect of the Ti/V atomic ratio on the isopropyl alcohol conversion reaction product yields over Ti-V-O catalysts at 250°C. As shown in Figure 2, with increasing titanium

concentration in the catalyst composition, the yields of acetone and propylene and the conversion of isopropyl alcohol pass through a maximum at the Ti-V=5-5 sample. On this catalyst, the outputs of acetone and propylene are 17% and 51%, and the isopropanol conversion reaches 68%.

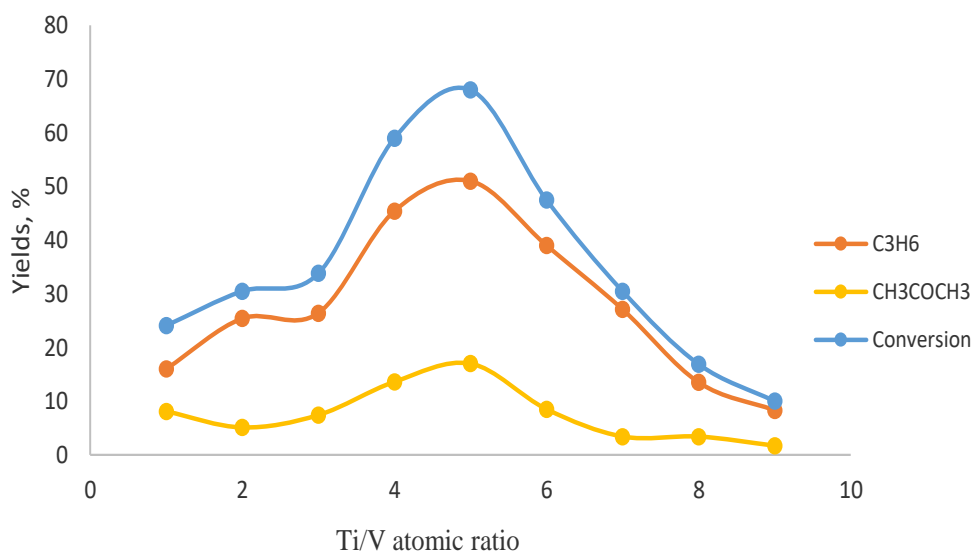


Figure 2. Activity dependence of Ti-V-O catalytic system in isopropanol dehydrogenation reaction on the Ti/V atomic ratio. T =250°C

In contrast to low reaction temperatures, at higher temperatures, the conversion of isopropanol over samples of the Ti-V-O catalytic system produces carbon dioxide in addition to acetone and propylene. Figure 3 shows the dependence of outputs of isopropyl alcohol conversion reaction products on the titanium to vanadium atomic ratio in the composition of the Ti-V-O catalytic system at a reaction temperature of 300°C. As seen from this figure, with increasing titanium concentration in the catalyst composition, the acetone yield tends to

decrease while the propylene yield increases. The exception is the catalyst Ti-V=5-5, which shows the highest propylene yield and isopropyl alcohol conversion.

The carbon dioxide output at 300°C on the studied catalysts does not exceed 2%, and it diminishes with the increase of titanium content in the catalyst. On samples rich in titanium, carbon dioxide is practically not formed.

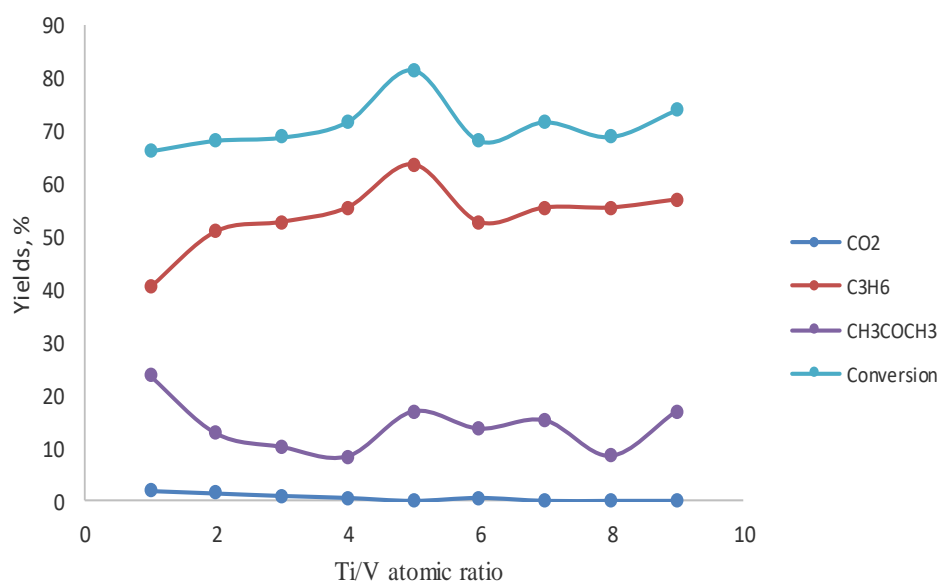


Figure 3. Activity dependence of Ti-V-O catalytic system in isopropanol dehydrogenation reaction on the Ti/V atomic ratio. T=300°

Summarizing the above, we can say that the main products of isopropanol alcohol conversion in the absence of oxygen on samples of the Ti-V-O catalytic system are acetone and propylene. The catalysts with an equimolar ratio of initial elements are active in the reaction of the formation of these products.

In the transformation of isopropanol in the presence of oxygen over catalysts of the Ti-V-O catalytic system, the reaction products are acetone, propylene carbon dioxide, and at high temperatures, destructive decomposition products.

Figure 4 shows the investigation results of the isopropanol oxidation reaction on the Ti-V=7:3

catalyst. As can be seen from the figure, the transformation of isopropanol starts at a temperature of 150°C with the formation of 26.5% acetone and 12% propylene. As the reaction temperature increases, the yields of both acetone and propylene pass through a maximum. The highest yield of acetone is reached at 200°C and is equal to 37.4%. The highest yield of propylene (55.3%) is observed at 300°C.

The formation of carbon dioxide, a by-product of the reaction, starts at 250°C and increases with increasing reaction temperature. At 400°C, its yield is 12.7%. Figure 4 also shows that on the Ti-V=7-3 catalyst, the conversion of isopropyl alcohol reaches about 83.8%.

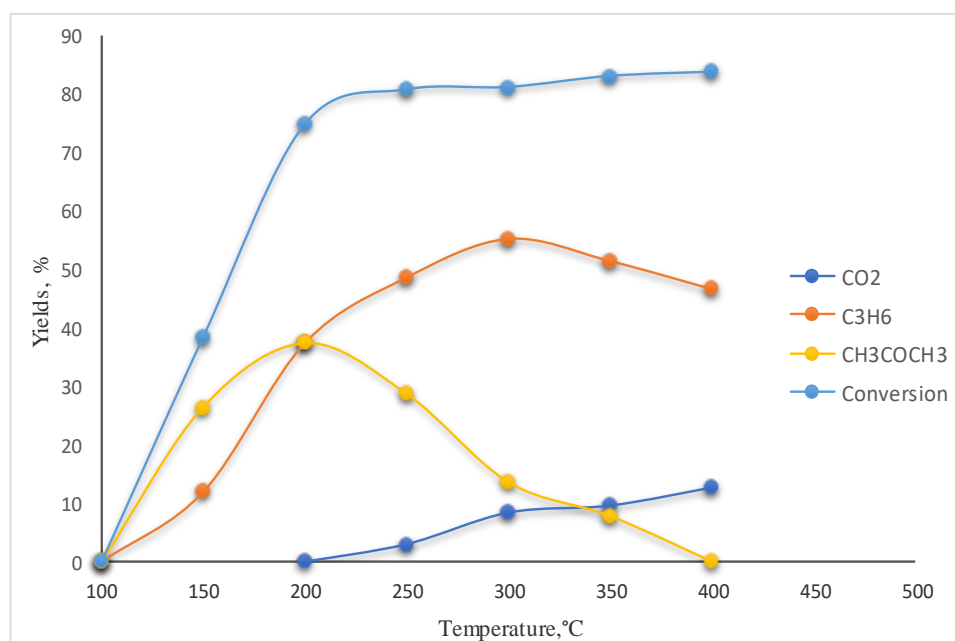


Figure 4. Temperature effect on the yields of isopropanol dehydrogenation reaction products in the presence of oxygen on catalyst Ti-V=7-3

The study results of the activity of all samples of the Ti-V-O catalytic system showed that their activity depends on the quantitative composition of the binary catalyst. Figure 5 shows the dependence of reaction product yields of isopropanol dehydrogenation in the presence of oxygen on the atomic ratio of Ti/V in the composition of binary Ti-V-O catalysts at a reaction temperature of 200°C. It can be seen that with increasing titanium concentration in the catalyst composition, the acetone yield slightly decreases to 20% and then passes through the maximum (37.4) on the catalyst

Ti-V=7-3. The propylene yield with rising titanium concentration in the catalyst composition passes through the maximal value at the catalyst Ti-V=3-7. Starting from the sample Ti-V=6-4, it increases to 45% at the sample Ti-V=9-1. The nature of the change in isopropyl alcohol conversion from catalyst composition is similar to the shift in acetone yield. On this catalytic system at 200°C, the conversion of isopropyl alcohol reaches 74.9%. As can be seen from Figure 5, the formation of deep oxidation product - carbon dioxide - is not observed in the studied samples.

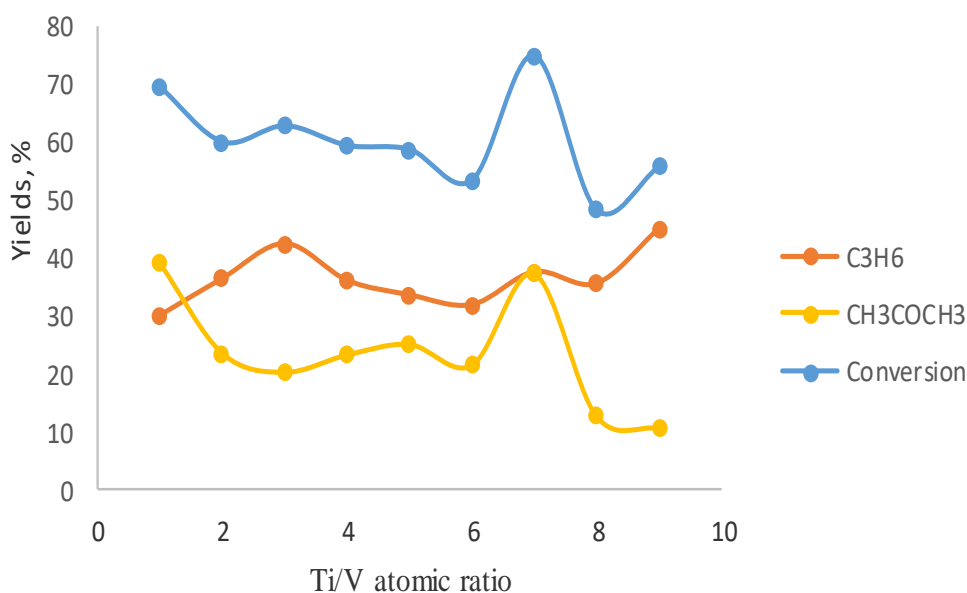


Figure 5. Activity dependence of Ti-V-O catalytic system in isopropyl alcohol dehydrogenation reaction in the presence of oxygen on the Ti/V atomic ratio. T=200°C

A different character of the effect of catalyst composition on its activity in the oxidative dehydrogenation reaction of isopropyl alcohol is obtained at temperatures above 300°C. The results of the study of the dependence of the reaction product yields of oxidative dehydrogenation of isopropyl alcohol over titanium-vanadium oxide catalysts on their composition at 350°C are shown in Figure 6. At 350°C, in addition to acetone and propylene, carbon dioxide and products of destructive decomposition formation in isopropyl alcohol oxidative dehydrogenation are observed in the reaction products. It can be seen that at 350°C, the yields of acetone and carbon dioxide depend on the atomic ratio of Ti/V, varying randomly in the range from 5

to 15%. This indicates that the acetone and carbon dioxide yields are not practically independent of the catalyst composition. The data shown in Figure 6 shows that, except for the catalyst Ti-V=1-9, all other samples have high activity in the propylene formation reaction. According to literature data, dehydration reactions of low-molecular-weight alcohols into the corresponding olefins proceed on acidic centers. Because vanadium oxide has an acidic nature on the surface, all titanium vanadium oxide catalysts except for the catalyst Ti-V=1-9 show high activity in the reaction of dehydration of isopropyl alcohol into propylene. The maximum conversion of isopropyl alcohol at 350°C on the studied catalysts reaches 92.3%.

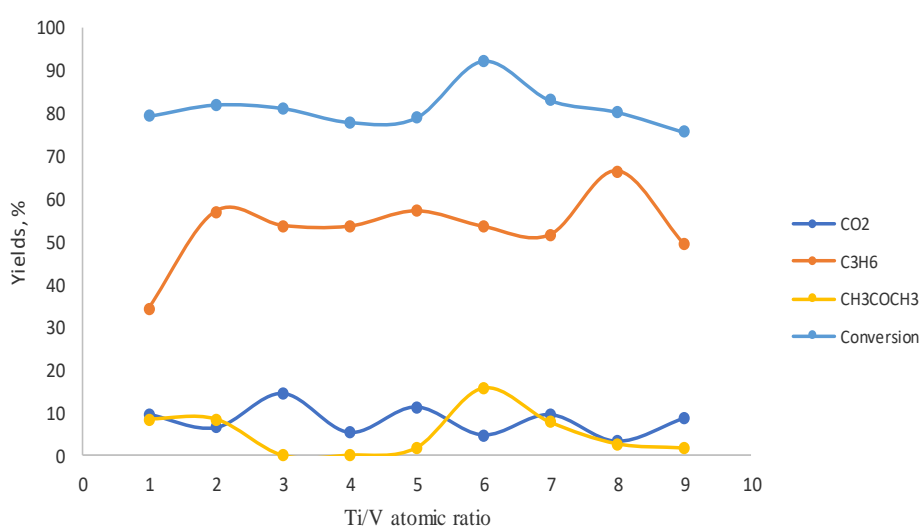


Figure 6. Activity dependence of Ti-V-O catalytic system in isopropyl alcohol dehydrogenation reaction in the presence of oxygen on the Ti/V atomic ratio. T=350°C

To evaluate the influence of surface acidity, we compared the activities of samples of the Ti-V-O catalytic system in isopropyl alcohol conversion

reactions and the reaction of butene-1 isomerization into trans and cis butenes-2. Figure 7 shows the dependence of the activity of samples of the Ti-V-O

catalytic system in the reaction of isopropanol dehydrogenation on the degree of isomerization of butene-1 into butenes-2. As can be seen from Figure 7 with increasing activity of samples of Ti-V-O catalytic system in the reaction of isomerization of butene-1 to butenes-2 (in other words, increasing the surface acidity of the catalyst), the outputs of propylene, acetone, and total conversion of isopropanol pass through the maximal value. This suggests that increasing the surface acidity leads to a rise in the yields of acetone and propylene. This allows us to say that a specific value of surface

acidity is necessary for a high conversion rate of isopropanol into propylene and acetone on titanium-vanadium oxide catalysts. This is because vanadium oxide has an acidic nature of the surface; increasing its content in the composition of binary titanium-vanadium oxide catalysts leads to an increase in the degree of butene-1 isomerization (respectively and surface acidity) from 45.3% on the sample Ti-V=9-1 to 70.54% on the sample Ti-V=1-9. In this connection, samples with high surface acidity are active in the reaction of isopropyl alcohol conversion to propylene and acetic acid.

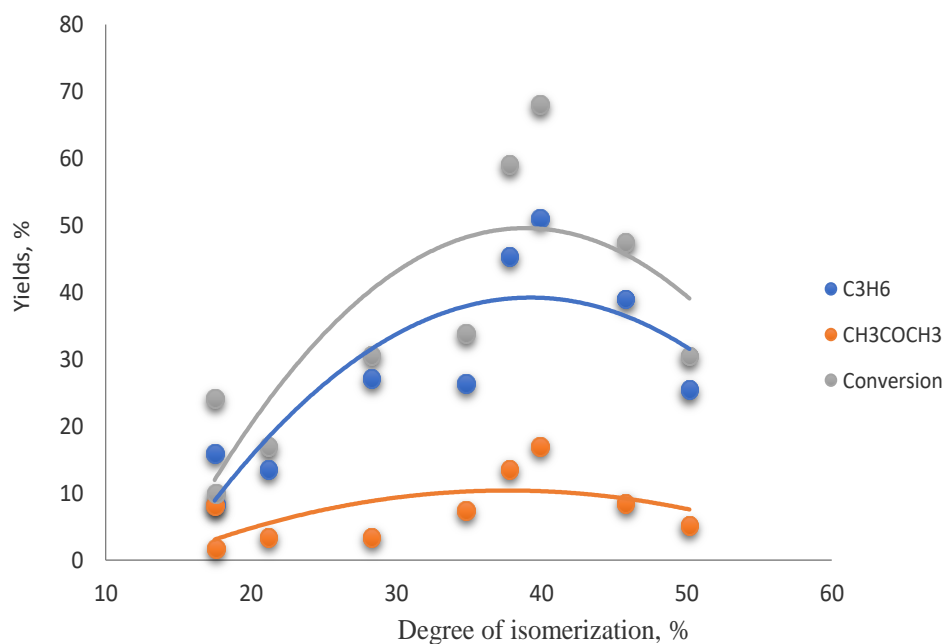


Figure 7. Activity dependence of Ti-V-O catalytic system samples in the reaction of isopropanol dehydrogenation on the surface acidity (degree of isomerization of butene-1 to butene-2). T=300°C

The effect of surface acidity (degree of isomerization of butene-1 to butenes-2) on the activity of the Ti-V-O catalytic system in the isopropanol

conversion reaction in the presence of oxygen is shown in Figure 8.

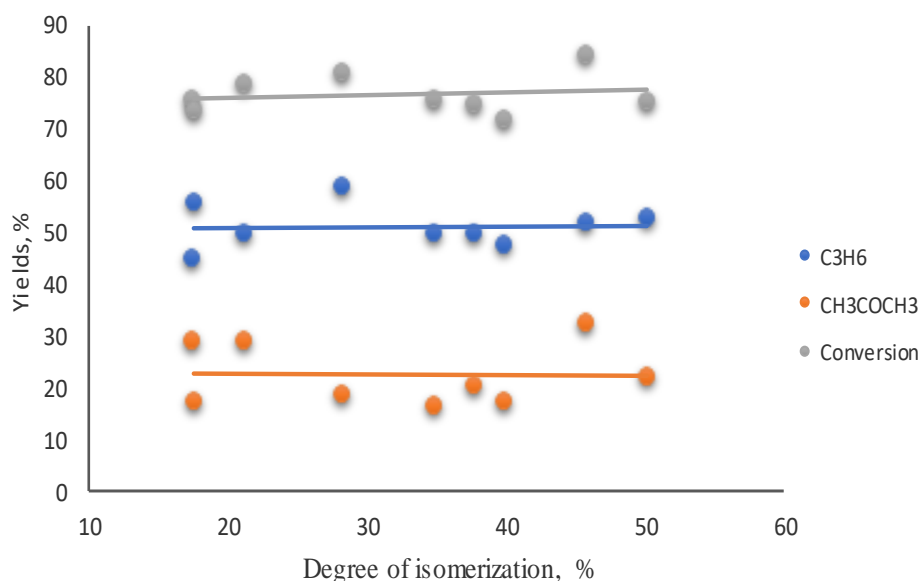


Figure 8. Activity dependence of Ti-V-O catalytic system samples in the oxidative dehydrogenation reaction of isopropanol on the surface acidity (degree of isomerization of butene-1 to butene-2). T=300°C

Figure 8 shows that with increasing activity of titanium-vanadium oxide catalysts in the reaction of isomerization of butene-1 to butenes-2, the yields of acetone, propylene, and total conversion of isopropyl alcohol practically do not change. This indicates the absence of influence of acid centers of the Ti-V-O catalytic system on the reaction of oxidative dehydrogenation of isopropanol.

4. Conclusion

Based on the conducted research, the following conclusions can be made:

1. Acetone and propylene are the main products of isopropanol dehydrogenation reaction over binary Ti-V-O catalytic system. The catalysts with the equimolar ratio of initial elements are active in the reaction of the formation of these products;
2. In the oxidative dehydrogenation of isopropyl alcohol, except for the catalyst Ti-V=1-9, all other binary catalysts of the Ti-V-O catalytic system are highly active in the reaction of propylene formation.
3. Increasing surface acidity of Ti-V-O catalytic system samples increases acetone and propylene yield during the isopropanol dehydrogenation reaction.
4. Change in surface acidity of Ti-V-O catalytic system samples does not lead to a change in product yields during the isopropanol oxidative dehydrogenation reaction.

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