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INVESTIGATION OF THE ISOMERIZATION REACTION OF BUTENE-1 TO BUTENES-2 ON BINARY TUNGSTEN-CONTAINING CATALYSTS

K.X. Aghayeva, V.L. Baghiyev

Azerbaijan State Oil and Industry University
Azadlyg 20, Baku, AZ-1010, Azerbaijan
e-mail: vagif_bagiev@yahoo.com

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Abstract: *The activity of tungsten-containing catalysts in the reaction of isomerization of butene-1 to butenes-2 was studied in the work. The results obtained showed that the ^ introduction of the second element into the composition of the tungsten oxide catalyst had a different effect on its activity in the butene-1 isomerization reaction. It was established that an increase in the amount of molybdenum in the composition of a binary tungsten-containing catalyst at low temperatures leads to a decrease in the degree of butene-1 isomerization while at high temperatures it leads to an increase in the rate of butene-1 isomerization. It found that the addition of titanium to the composition of the tungsten oxide catalyst leads to an increase in the butene-1 isomerization rate. When copper is added to the composition of the tungsten oxide catalyst, the total yield of butene-2 passes through a maximum, and on samples rich in copper, the isomerization of butene-1 practically does not occur. It revealed that the activity of binary tungsten oxide catalysts in the isomerization reaction of butene-1 to butenes-2 changes in the following order: Ti-W-O > Mo-W-O > Cu-W-O.*

Keywords*: isomerization, butene-1, butenes-2, binary catalyst, acidity*
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Introduction

As is known from periodic literature, catalysts based on tungsten oxide exhibit high activity in the reactions of hydrogen production [1], deep [2] and partial oxidation of organic compounds [3]. Also, catalytic systems based on elements such as molybdenum, titanium, and copper are often used as catalysts for ethanol conversion reactions. In this regard, we studied the effect of additions of molybdenum, titanium, and copper on the activity of binary tungsten oxide catalysts in the ethanol oxidation reaction. Studies showed that on molybdenum-tungsten oxide catalysts rich in molybdenum, the reaction of dehydration of ethanol to ethylene occurs, while samples enriched in tungsten are active in the reaction of oxidative dehydrogenation of ethanol to acetaldehyde [4]. On titanium–tungsten oxide catalysts, the main product of ethanol conversion at temperatures up to 300°C is diethyl ether, while at a higher temperature, the reaction of ethanol dehydration to ethylene proceeds [5]. Ethylene formation is observed on samples rich in titanium, while samples rich in tungsten are active in the reaction of formation of diethyl ether. At temperatures up to 300°C, acetaldehyde is practically the only product of ethanol oxidation over copper–tungsten oxide catalysts [6]. It is known that the acid–based properties of the surface of heterogeneous catalysts quite often correlate with their catalytic properties [7–9]. To characterize the acid–base properties of a surface under conditions close to real catalytic reactions, some catalytic reactions are widely used as model ones [10, 11]. With that end in view, such reactions as dehydration of propanol-2, butanol-2, isomerization of olefins, etc. are used [12-14]. In recent years, due to the ease of implementation, the acid–base properties of oxide catalysts are often characterized by

measuring their activity in the isomerization of butene-1 to cis and trans butenes-2 [15, 16]. In this regard, in this work, to assess the acidic properties of the surface of binary tungsten-containing catalysts, we studied their activity in the isomerization reaction of butene-1 into butenes-2.

Experimental Part

Molybdenum-tungsten, titanium-tungsten, and copper-tungsten oxide catalysts were prepared by coprecipitation from aqueous solutions of ammonium molybdate, copper nitrate, titanium tetrachloride, and ammonium tungsten. The resulting mixture was evaporated and dried at 95-100°C, decomposed to complete release of nitrogen oxides and chlorine at a temperature of about 250-300°C. The obtained solid mass was calcined at a temperature of 700°C for 10 hours. Thus, we have prepared 27 catalysts that meet the following conditions:
mA/nB, where A is Mo, Ti, Cu; B - W,
m,n=1÷9, m+n=10.

The isomerization reaction of butene-1 to butene-2 was carried out at a feed space velocity of 1200 h-1, in the temperature range of 150–400°C. The reactor was loaded with 5 ml of a catalyst with grains of 1–2 mm, and a reaction mixture of butene-1 and nitrogen was fed. The ratio of butene-1 to nitrogen was 1:9. The analysis of the mixture of unreacted butene-1 and the formed trans and cis butenes-2 was carried out by the chromatographic method using a column 5 meters long filled with celite coated with Vaseline oil.

Results and discussion

The results of the study of the isomerization of butene-1 to butenes-2 on molybdenum-tungsten oxide catalysts showed that on the Mo-W=1-9 catalyst, isomerization of butene-1 begins at a temperature of 200°C with the formation of 2.2% trans-butene-2 and 2.8% cis-butene-2, while the conversion of butene-1 is 5%. With an increase in the reaction temperature over the entire temperature range studied, the yields of butenes-2 increase, and at a reaction temperature of 400°C, the total yield of trans and cis butenes-2 reaches 30.2%. Similar results are obtained for other samples. It was also found that the total yield of 2-butenes on all the studied catalysts does not exceed 52%.

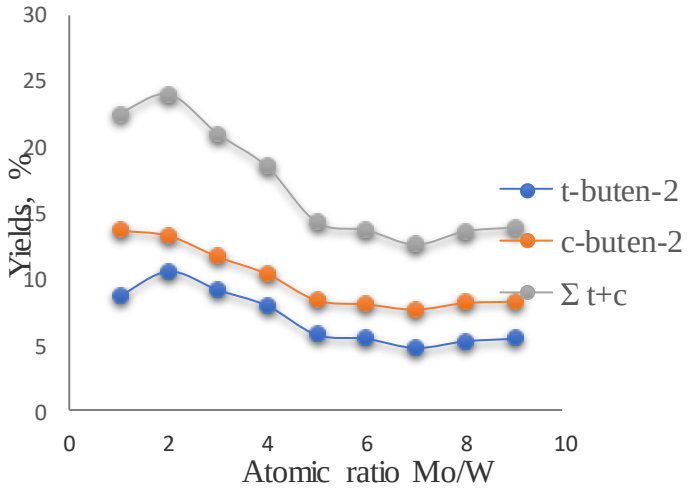

Fig. 1. Dependence of the yields of trans and cis-butenes-2 on the atomic ratio of molybdenum to tungsten. T = 350°C.

The ratio of the yields of trans and cis isomers of butene-2 on the studied catalysts varies within 0.55 – 0.85. The data obtained make it possible to say that the rate of butene-1 isomerization at different temperatures depends differently on the atomic ratio of molybdenum to tungsten.

Figure 1 shows the dependence of the yields of trans and cis butenes-2 on the atomic ratio of molybdenum to tungsten at a temperature of 350°C. As can be seen from Figure 1, with an increase in the amount of molybdenum in the composition of the binary catalyst, the yields of butenes-2 decrease and, on samples rich in molybdenum, does not exceed 14%. Such dependences are observed at temperatures up to 350°C.

A different picture is observed at a temperature of 400°C. The dependences of the yields of trans and cis butenes-2 on the atomic ratio of molybdenum to tungsten at a temperature of 400°C are shown in Figure 2. As is seen from Fig. 2, in contrast to lower temperatures at 400°C, with an increase in the amount of molybdenum in the binary catalyst 2 increases from 30% on Mo-W=1-9 catalyst to 52% on samples rich in molybdenum.

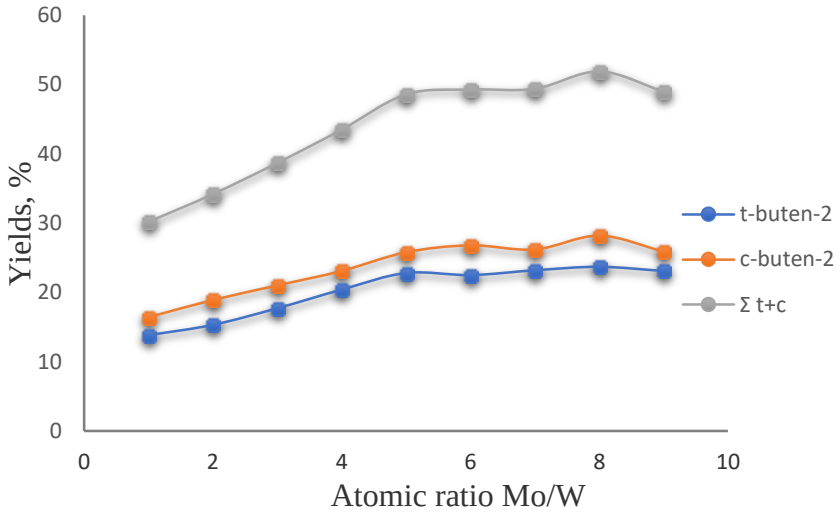

Fig. 2. Dependence of the yields of trans and cis butenes-2 on the atomic ratio of molybdenum to tungsten. T = 400°C.

It is assumed in [17] that the total acidity of the surface is determined by the total rate of butene-2 formation. At the same time, the formation of trans-butene-2 occurs at Brönsted centers, while the formation of cis-butene-2 occurs at Lewis acid centers. Thus, the results obtained make it possible to insist that the rate of isomerization of butene-1 (total acidity of the surface) on molybdenum-tungsten oxide catalysts increases with increasing reaction temperature. An increase in the content of molybdenum in the composition of the catalyst leads at low temperatures to a decrease in the total acidity of the surface (the rate of butene-1 isomerization decreases), while at temperatures above 400°C it leads to an increase in the rate of butene-1 isomerization, which indicates to an increase in the total acidity of the surfaces. Also, from the data obtained, it can be said that on the surface of molybdenum-tungsten oxide catalysts, the number of Lewis centers is greater than the number of Brönsted centers, since the ratio of the yields of trans and cis isomers of butene-2 is less than unity and varies within 0.55–0.85.

As distinct from the previous series of catalysts, isomerization of butene-1 on titanium-tungsten oxide catalysts starts at a temperature of 150°C. Thus, 4.2% cis-butene-2 is formed on the Ti-W=1-9 catalyst at 150°C. With an increase in the reaction temperature, the yields of butenes-2 increase sharply and at a reaction temperature of 350°C reach their maximum value (63.6%). Approximately similar

dependences are obtained for other samples. The highest yield of 2-butenes on the studied catalysts reaches 89.1%. The ratio of the yields of trans and cis isomers of butene-2 on the studied catalysts varies within 0.4 – 1.14. It ought to be noted that on samples rich in tungsten, the ratio of the yields of trans and cis isomers is much lower than unity, while on samples rich in titanium this value varies in the range of 1 - 1.15. The obtained data allow us to state that at temperatures up to 300°C, the yields of butene-1 isomerization products grow as titanium in the catalyst composition grows, while at higher temperatures the dependence of the isomerization rate on the atomic ratio of titanium to tungsten has the form of a curve with two maxima. Fig.3 shows the dependence of the yields of trans and cis butenes-2 on the atomic ratio of titanium to tungsten at a temperature of 250°C.

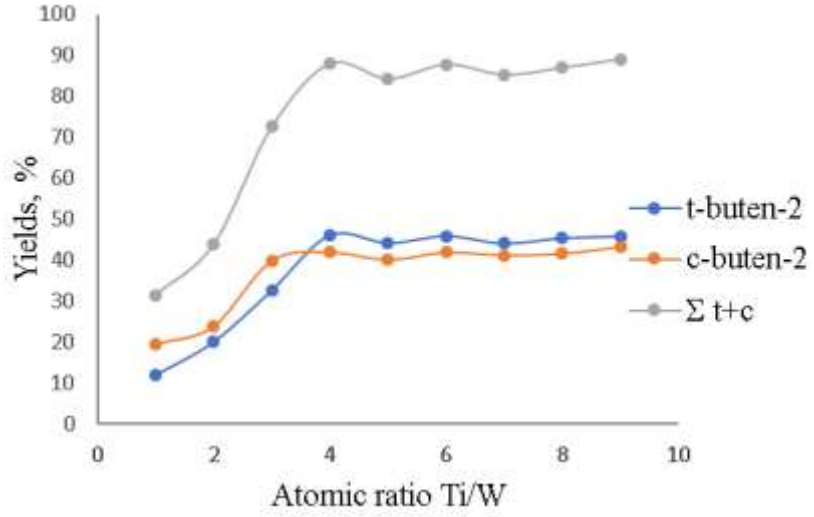

Fig. 3. Dependence of the yields of trans and cis butenes-2 in the isomerization of butene-1 on the atomic ratio of titanium to tungsten. T = 250°C.

As can be seen from Figure 3, with an increase in the amount of titanium in the composition of the binary catalyst, the yields of butenes-2 increase from 31.5% on the Ti-W=1-9 catalyst to 89.1% on the Ti-W=9-1 sample. Such dependences are observed at temperatures up to 300°C. A different picture is observed at temperatures above 300°C.

Fig.4 shows the dependence of the yields of trans and cis butenes-2 on the atomic ratio of titanium to tungsten at a temperature of 350°C.

As can be seen from Fig. 4, the dependence of butene-2 yields on the atomic ratio of titanium to tungsten has the form of a curve with two maxima on samples Ti-W=4-6 and Ti-W=6-4.

The obtained results show that the rate of the isomerization reaction of butene-1 on titanium-tungsten oxide catalysts increases as reaction temperature increases. An increase in the content of titanium in the composition of the catalyst at low temperatures leads to an increase in the isomerization rate of butene-1. This means that the total acidity of the surface is increased, while at high temperatures, the relationship between the isomerization rate (total surface acidity) and the composition of the catalyst has the form of a curve with two maxima. In contrast to the previous catalytic system, the number of Lewis and Brönsted acid sites on the surface of titanium-tungsten oxide catalysts is approximately the same.

According to the data on the study of the activity of copper-tungsten oxide catalysts, the isomerization of butene-1 on the Cu-W=1-9 catalyst starts at a temperature of 200°C and 3.5% trans and cis butenes-2 are formed. The total yield of butenes-2 grows as temperature rises, and the maximum yield reaches 28.8% at 350°C. Approximately the same dependences are obtained for other samples. However, it should be noted that an increase in the amount of copper in the composition of the catalyst leads to a decrease in the yields of butenes-2 and a shift in their formation towards higher temperatures. Thus, on the Cu-W=9-1 sample,

the formation of butenes-2 is observed at a temperature of 400°C, and their total yield does not exceed 2.4%. It can be seen from the results obtained that the ratio of the yields of trans and cis isomers of butene-2 on the studied catalysts, with rare exceptions, varies from 0.2 to 0.6. Based on the data obtained, it can be concluded that with a change in the atomic ratio of copper to tungsten, the total yield of butenes-2 at all studied temperatures passes through a maximum.

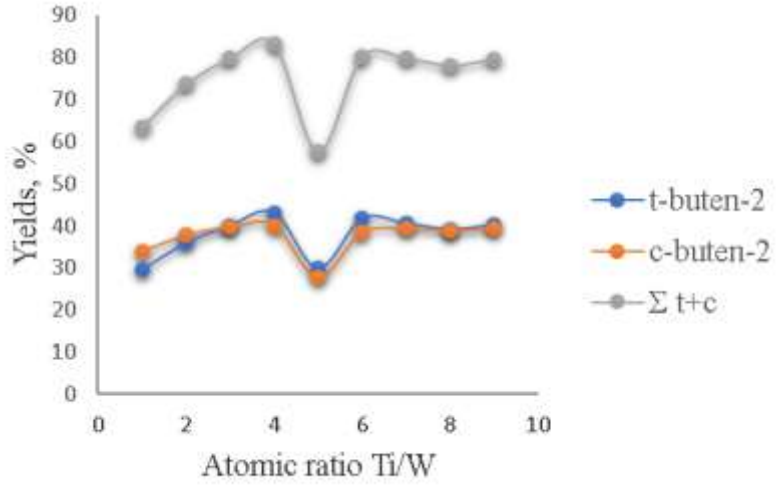

Fig. 4. Dependence of the yields of trans and cis butenes-2 in the butene-1 isomerization reaction on the atomic ratio of titanium to tungsten. T = 350°C.

The dependence of the yields of trans and cis butenes-2 on the atomic ratio of copper to tungsten at a temperature of 300°C is shown in Fig. 5.which shows that with an increase in the amount of copper in the composition of the binary catalyst, the yields of butenes-2 pass through a maximum on the Cu-W catalyst =3-7. A further increase in copper in the composition of the binary copper-tungsten oxide catalyst leads to a decrease in the yields of butenes-2, and on samples starting from Cu-W=7-3 at this temperature, butene-1 isomerization does not occur.

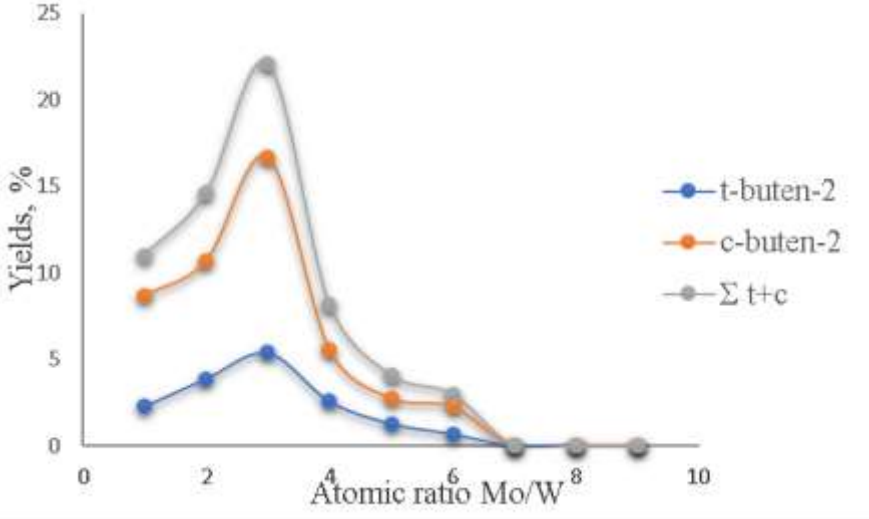

Fig. 5. Dependence of the yields of trans and cis butenes-2 in the butene-1 isomerization reaction on the atomic ratio of copper to tungsten. T = 300°C.

At temperatures above 400°C, the formation of 2-butenes is observed in all the studied samples. Fig. 6 shows the dependence of the yields of trans and cis butenes-2 on the atomic ratio of copper to tungsten at a temperature of 400°C. As can be seen from Fig. 6, the dependence of butene-2 yields on the atomic ratio of copper to tungsten has the form of a curve with a maximum on the Ti-W=3-7 sample. On this sample, the maximum yield of butenes-2 reaches 57%.

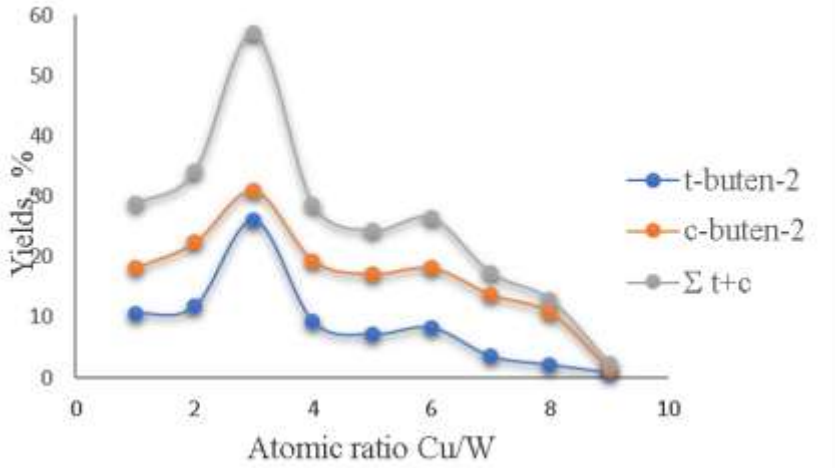

Fig. 6. Dependence of the yields of trans and cis butenes-2 in the butene-1 isomerization reaction on the atomic ratio of copper to tungsten. T = 400°C.

The results obtained allow us to say that the total acidity of the surface on copper-tungsten oxide catalysts increases as the reaction temperature increases. With an increase in the content of copper in the composition of the catalyst, the total acidity of the copper-tungsten oxide catalysts passes through a maximum on the Ti-W=3-7 sample and on samples with a high copper content is almost zero. It can also be said from the obtained data that the number of Lewis centers on the surface of copper–tungsten oxide catalysts is much higher than the number of Brönsted centers, since the ratio of the yields of trans and cis isomers of butene-2 is less than unity and varies from 0.2 to 0.6.

Based on the obtained results, it can be said that the introduction of the second element into the composition of the tungsten oxide catalyst has a different effect on their activity in the butene-1 isomerization reaction and, accordingly, on their acidity. Thus, an increase in the amount of molybdenum in the composition of a binary tungsten containing catalyst at low temperatures results in a decrease in the total surface acidity, while at high temperatures it leads to an increase in the total surface acidity. As for the Ti-W-O catalytic system, the addition of titanium to the composition of the tungsten oxide catalyst leads to an increase in the total acidity of the surface. When copper is added to the composition of the tungsten oxide catalyst, the total acidity of the surface passes through a maximum, and acid sites are practically absent on copper-rich samples.

The total acidity of binary tungsten oxide catalysts in the following order:

Ti-W-O > Mo-W-O > Cu-W-O

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BİNAR VOLFRAM TƏRKİBLİ KATALİZATORLARDA BUTEN-1-İN BUTEN-2-YƏ İZOMERLƏŞMƏ REAKSİYASININ TƏDQİQİ

K.X. Ağayeva, V.L. Bağıyev

Azərbaycan Dövlət Neft və Sənaye Universiteti
Azadlıq 20, Bakı, AZ-1010, Azərbaycan
e-mail: vagif_bagiev@yahoo.com

Xülasə: İşdə buten-1-in buten-2-yə izomerləşməsi reaksiyasında volfram tərkibli katalizatorların aktivliyi öyrənilmişdir. Alınan nəticələr göstərmişdir ki, ikinci elementin volfram oksidinə əlavə edilməsi katalizatorunun izomerləşmə reaksiyasında aktivliyinə fərqli təsir edir. Müəyyən edilmişdir ki, aşağı temperaturlarda binar volfram tərkibli katalizatorun tərkibində molibden miqdarının artması buten-1-in izomerləşmə dərəcəsinin azalmasına, yüksək temperaturda isə artmasına səbəb olur. Göstərilmişdir ki, titanın volfram oksidinə əlavə edilməsi katalizatorun buten-1 izomerləşmə sürətinin artmasına səbəb olur. Mis volfram oksidinə əlavə etdikdə isə katalizatorun buten-2-in izomerləşmə reaksiyasında aktivliyi maksimumdan keçir və mislə zəngin nümunələrdə buten-1-in izomerləşməsi praktiki olaraq baş vermir. Müəyyən edilmişdir ki, buten-1-in buten-2-yə izomerləşmə reaksiyasında binar volfram oksid katalizatorlarının aktivliyi aşağıdakı ardıcıllıqla dəyişir: Ti-W-O > Mo-W-O > Cu-W-O.
Açar sözlər: izomerləşmə, butenl-1, butenlər-2, binar katalizator, turşuluq.

ИССЛЕДОВАНИЕ РЕАКЦИИ ИЗОМЕРИЗАЦИИ БУТЕНА-1 В БУТЕНЫ-2 НА БИНАРНЫХ ВОЛЬФРАМСОДЕРЖАЩИХ КАТАЛИЗАТОРАХ

К.Х. Агаева, В.Л. Багиев

Азербайджанский Государственный Университет Нефти и Промышленности
Азадлыг 20, Баку, AZ-1010, Азербайджан
e-mail: vagif_bagiev@yahoo.com

Аннотация: В работе изучена активность вольфрамсодержащих катализаторов в реакции изомеризации бутена-1 в бутены-2. Полученные результаты показали, что введение второго элемента в состав вольфрам оксидного катализатора по-разному влияет на их активность в реакции изомеризации бутен-1. Установлено что увеличение количества молибдена в составе бинарного вольфрамсодержащего катализатора при низких температурах приводит к уменьшению степени изомеризации бутена-1, в то время как при высоких температурах способствует росту скорости изомеризации бутена-1. Показано, что добавление титана в состав вольфрам оксидного катализатора приводит к росту скорости изомеризации бутена-1. При добавлении же меди в состав вольфрам оксидного катализатора суммарный выход бутенов-2 проходит через максимум и на образцах богатых медью процесс изомеризации бутена-1 практически не протекает. Найдено, что активность бинарных вольфрам оксидных катализаторов в реакции изомеризации бутена-1 в бутены-2 изменяется в следующем порядке: Ti-W-O > Mo-W-O > Cu-W-O.
Ключевые слова: изомеризация, бутен-1, бутены-2, бинарный катализатор, кислотность.