

UDC 544.473-039.61

**DEPENDENCE OF ACTIVITY OF BINARY Mo-V-O CATALYSTS IN THE REACTION OF DEHYDROGENATION AND OXIDATION OF ISOPROPYL ALCOHOL ON ACIDIC SURFACE PROPERTIES****N.I. Aghayeva, S.A. Mammadkhanova**

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Received 15 08.2023

Accepted 27.10.2023

**Abstract.** The reaction of dehydrogenation and oxidative dehydrogenation of isopropyl alcohol on molybdenum-vanadium oxide catalysts has been studied. It found that the dependences of isopropyl alcohol conversion and propylene yields on the atomic ratio of molybdenum to vanadium in reaction of dehydrogenation of isopropyl alcohol have the form of a curve with two maxima on samples Mo-V=2-8 and Mo-V=6-4. To characterize the acidic properties of the surface of molybdenum-vanadium oxide catalysts, their activity in the reaction of butene-1 isomerization into butenes-2 was also studied.

It showed that on molybdenum-vanadium catalysts the dependence of the yield of 2-butenes on the ratio of molybdenum to vanadium also had the form of a curve with two maxima. The activities of molybdenum-vanadium oxide catalysts were compared with their acidic properties. It revealed that on binary molybdenum-vanadium oxide catalysts in the reaction of isopropyl alcohol dehydrogenation the increase of surface acidity led to the increase in acetone yield and the decrease in propylene yield. In the reaction of oxidative dehydrogenation of isopropyl alcohol, the increase in surface acidity led to the increase in acetone yield, while propylene yield practically did not change.

**Keywords:** isopropyl alcohol, dehydrogenation, oxidative dehydrogenation, vanadium oxide, isomerization, surface acidity.

**DOI:** 10.32737/2221-8688-2023-4-388-395

### Introduction

Isopropanol is an important renewable raw material derived from bioresources. The direct conversion products of isopropyl alcohol are acetone, propylene and various esters. Catalytic systems based on elements such as molybdenum, titanium and vanadium, etc. are often used as catalysts for isopropyl alcohol conversion reactions. [1-3]. We studied the activity of binary molybdenum-vanadium oxide catalysts in the dehydrogenation and oxidative dehydrogenation reactions of isopropyl alcohol [4,5].

It is known that in the heterogeneous catalysis, the acid-base properties of solid catalysts affect the activity and selectivity of many catalytic reactions, not only in acid-base transformations, but also in the reduction and

oxidation reactions [6,7]. There are numerous catalytic reactions activated by solid acid catalysts, which are widely used in the petroleum refining and chemical industry [8,9].

The acid-base properties of solid catalysts have been discussed in detail over the years, however, no clear and generalized correlations with catalytic properties have been unequivocally established. The main reason was that physical methods to establish the acid-base characteristics of catalysts were usually performed at room temperature or slightly above and mostly under conditions very far from true catalytic conditions, sometimes even under vacuum. Therefore, some catalytic reactions were chosen as a model to try to characterize the acid-base properties under

conditions as close as possible to real catalytic reactions [10, 11]. To characterize the acid-base properties of oxide catalysts under conditions close to catalytic ones, the reaction of butene-1 isomerization into cis and trans butenes-2 have been used quite often in recent years because of its simplicity [12-14].

### Experimental part

Binary molybdenum-vanadium oxide catalysts of different compositions were prepared by co-precipitation from aqueous solutions of ammonium molybdenum acid and ammonium metavanadate. The obtained mixtures were evaporated at 95-100°C, then the formed precipitates were dried at 100-120°C and finally decomposed to complete release of nitrogen oxides at a temperature of about 250°C. The obtained solid masses were calcined at 700°C for 10 hours. Thus, 9 catalysts with atomic ratio of elements from Mo:V=1:9 to Mo:V=9:1 were synthesized.

The catalytic activity of the synthesized samples in the reactions of dehydrogenation and oxidation of isopropyl alcohol was investigated on a flow unit with a tubular reactor in the temperature range of 150-450°C. The volumetric feed rate of the feedstock was 1200 h<sup>-1</sup>. The ratio of starting reagents in the isopropyl alcohol dehydrogenation reaction was isopropyl alcohol: nitrogen = 1: 9, and in the

In the present work we have studied the dependence of the activity of binary molybdenum-vanadium oxide catalysts in the reaction of isopropyl alcohol dehydrogenation on their acidity, for the measure of which we chose the reaction rate of butene-1 isomerization into butenes-2.

isopropyl alcohol oxidation reaction was isopropyl alcohol: air = 1: 9. The yields of isopropyl alcohol conversion products, as well as the amount of unreacted alcohol were established on a chromatograph with a flame ionization detector and a 2 m long column filled with specially treated Polysorb-1 sorbent. The amount of formed carbon dioxide was determined on a chromatograph with a 6-meter column filled with Celite sorbent with vaseline oil applied on it.

The surface acidity of binary molybdenum-vanadium oxide catalysts was established by their activity in the test reaction of butene-1 isomerization into trans- and cis butenes-2. The butene-1 isomerization reaction was carried out in a tubular reactor in the temperature range of 150-450°C. The feedstock feed rate was 1200 h<sup>-1</sup>. The ratio of initial reagents in the isomerization reaction was butene-1 : nitrogen = 1: 9.

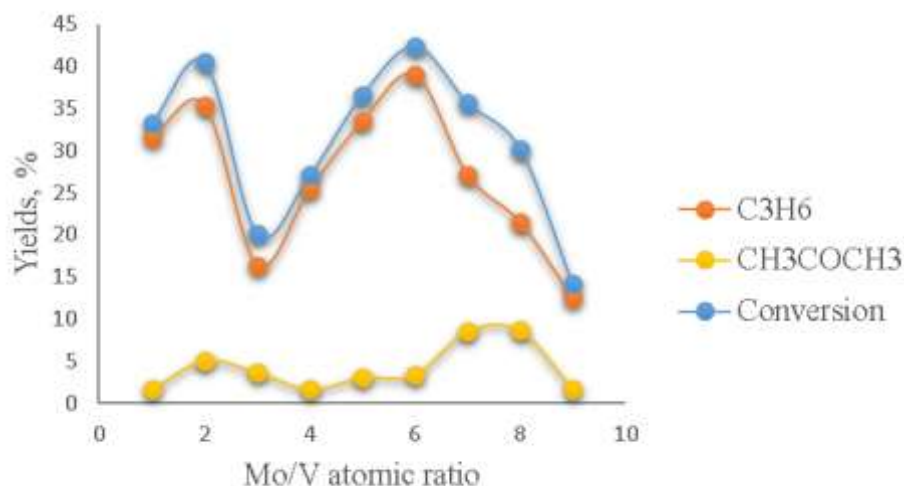
### Results and discussion

The products of isopropyl alcohol conversion reaction in the absence of oxygen on binary molybdenum-vanadium oxide catalysts are acetone, propylene, carbon dioxide and at high temperatures there are products of destructive decomposition of isopropyl alcohol.

The studies have shown that the reaction of isopropyl alcohol dehydrogenation on Mo-V-O catalysts starts from the temperature of 150°C. As the reaction temperature increases, the yields of propylene and acetone pass through a maximum. The activity of Mo-V-O catalysts also depends on their composition. Fig.1 shows the dependence of the activity of molybdenum-vanadium catalysts on their composition in the reaction of isopropyl alcohol dehydrogenation at 200°C. It can be seen that on

all catalysts the main product of the reaction is propylene and acetone. Dependences of isopropyl alcohol conversion and propylene yields on the atomic ratio of molybdenum to vanadium have the form of a curve with two maxima on the samples Mo-V=2-8 and Mo-V=6-4. Fig. 1 also shows that the highest acetone yield is observed at the Mo-V=8-2 sample.

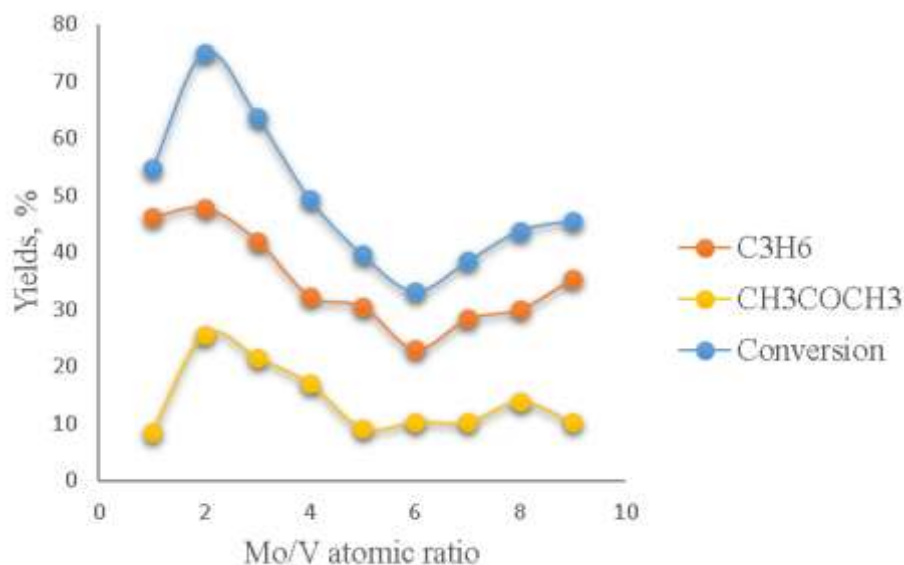
At isopropyl alcohol conversion in the presence of oxygen on molybdenum-vanadium catalytic system the reaction products are the same products as at isopropyl alcohol conversion in the absence of oxygen, namely acetone, propylene, carbon dioxide and products of destructive decomposition.



**Fig. 1.** Dependence of activity of molybdenum-vanadium oxide catalysts in isopropyl alcohol conversion in the absence of oxygen on their composition.  $T=200^{\circ}\text{C}$ .

Comparison of the activity of all molybdenum-vanadium oxide catalysts showed that their activity strongly depends on the atomic ratio of molybdenum to vanadium in the composition of the binary catalyst. The dependence of the activity of molybdenum-vanadium oxide catalysts on their composition in the oxidation reaction of isopropyl alcohol at  $200^{\circ}\text{C}$  is shown in Figure 2. As can be seen from this, the acetone yield with increasing atomic ratio of molybdenum to vanadium first

increases to 25.7% on the catalyst Mo-V=2-8, then decreases to 9.1% on the sample Mo-V=5-5 and finally practically does not change. The figure also shows that the propylene yield with increasing amount of molybdenum in the binary catalyst first decreases to 23.1% on Mo-V=6-4 sample and then increases to 35.4% on Mo-V=9-1 sample. It is also evident from the data obtained that no carbon dioxide formation is observed at  $200^{\circ}\text{C}$  on the studied catalysts.



**Fig. 2.** Dependence of activity of molybdenum-vanadium oxide catalysts in isopropyl alcohol conversion in the presence of oxygen on their composition.  $T = 200^{\circ}\text{C}$ .

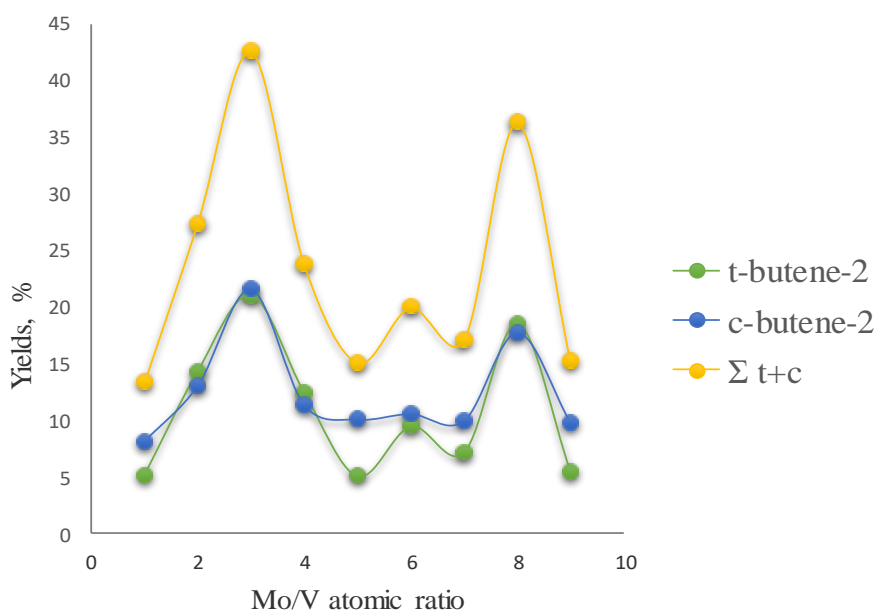
Figure 2 also shows that the yield of acetone for the samples with predominance of molybdenum does not depend much on the atomic ratio of molybdenum to vanadium, while on the samples with predominance of vanadium its maximum yield is observed on the sample Mo-V=2-8. Thus, vanadium-rich catalysts are active in the reaction of oxidative dehydrogenation of isopropyl alcohol into acetone and in the reaction of dehydration of isopropyl alcohol into propylene.

From the data shown in Fig. 2 we can also say that at 200°C the maximum conversion of ethanol on the studied samples reaches up to 75%.

The study of butene-1 to butene-2 isomerization reaction on molybdenum-vanadium oxide catalysts of different composition showed that butene-1 isomerization starts at 150°C on all studied molybdenum-vanadium oxide catalysts. As the temperature increases, the yield ratio of trans- and cis-butene-2 on the studied catalysts increases significantly from 0.40% at 200°C to 0.94% at

350°C.

Fig. 3 shows the yields of trans- and cis-butenes-2 as a function of the atomic ratio of molybdenum to vanadium. It can be seen that on molybdenum-vanadium catalysts the dependence of butenes-2 yields takes the form of a curve with two maxima. The first maximum is observed in the Mo-V=3-7 catalyst, and the second maximum is observed in the Mo-V=8-2 catalyst. These catalysts show high activity in the isomerization reaction. Our earlier X-ray diffraction studies revealed that different phases are formed in the Mo-V-O catalytic system. Thus, in the ratios of 1Mo/9V, 2Mo/8V, 3Mo/7V, 8Mo/2V and 9Mo/1V, three phases are formed: MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> and Mo<sub>2,4</sub>V<sub>3,6</sub>O<sub>16</sub>. In addition to molybdenum and vanadium oxides, other phases of complex composition are also formed at component ratios of 4Mo/6V, 5Mo/5V and 6Mo/4V. The formation of Mo<sub>2,4</sub>V<sub>3,6</sub>O<sub>16</sub> phase is apparently responsible for the activity of binary Mo-V-O catalysts in the reaction of butene-1 isomerization into trans and cis butenes-2.



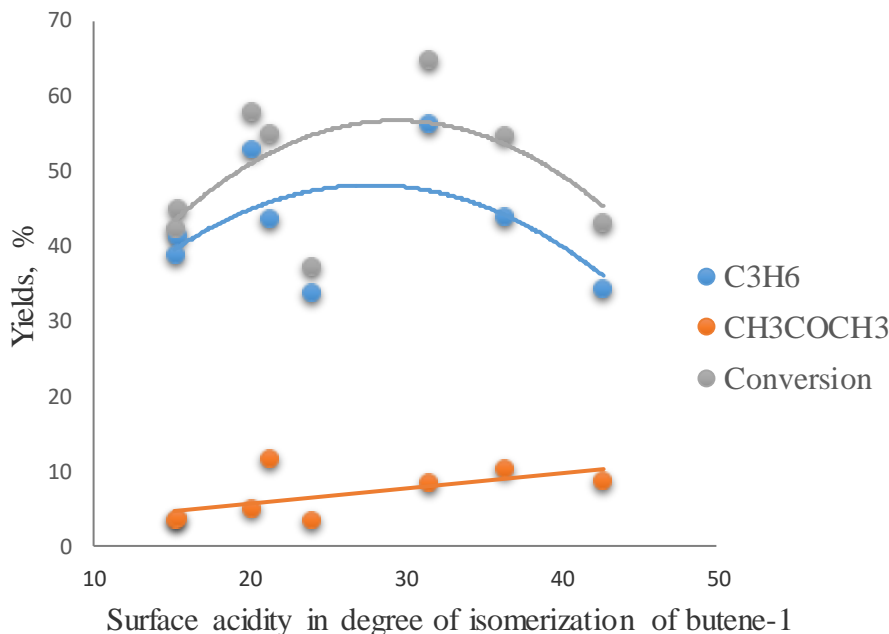
**Fig. 3.** Effect of molybdenum to vanadium ratio on the yield of isomerization products of butene-1. T=250°C

Fig.4 shows the dependence of acetone, propylene and isopropyl alcohol conversion yields in the reaction of isopropyl alcohol dehydrogenation on binary molybdenum-vanadium oxide catalysts on the acidity of the surface expressed in the degree of isomerization

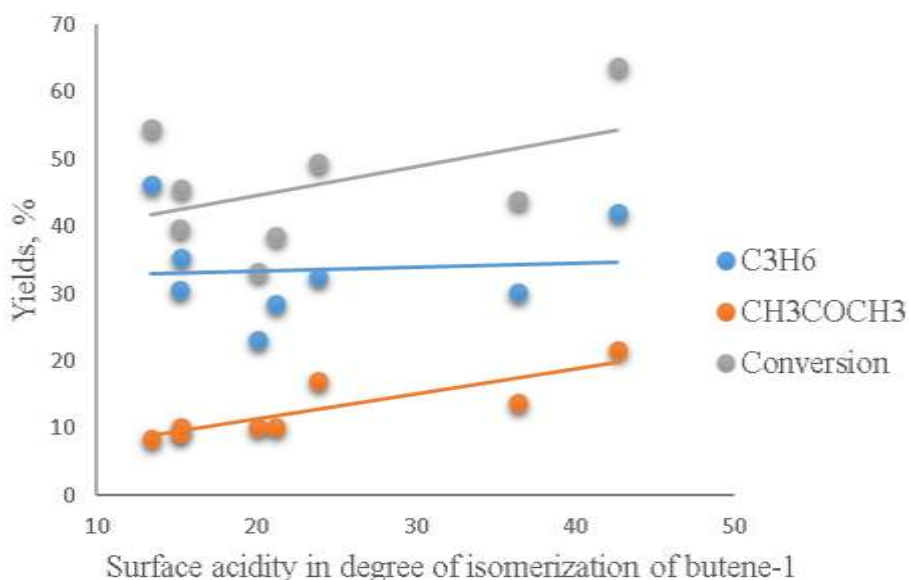
of butene-1 to butenes-2. As can be seen from Fig. 4, as surface acidity of molybdenum-vanadium oxide catalysts increases, the acetone yield increases as well, while the propylene yield and total conversion of isopropyl alcohol passes through a maximum. This suggests that

the increase in surface acidity leads to the increase in the reaction rate of dehydrogenation of the starting alcohol into acetone. On the other hand, for high rate of conversion of isopropyl alcohol to propylene on molybdenum-vanadium oxide catalysts, an average value of surface

acidity is necessary. Based on the results obtained, it can be said that the dehydrogenation reaction of isopropyl alcohol into acetone proceeds on strong acid centers and the formation of propylene on acid centers of average strength.



**Fig. 4.** Dependence of activity of molybdenum-vanadium oxide catalysts in the reaction of isopropyl alcohol dehydrogenation on surface acidity expressed in the degree of isomerization of butene-1 into butenes-2. T=250°C.



**Fig. 5.** Dependence of activity of molybdenum-vanadium oxide catalysts in the oxidative dehydrogenation reaction of isopropyl alcohol on surface acidity expressed in the degree of isomerization of butene-1 into butenes-2. T=250°C.

Dependences of acetone, propylene yields and feedstock conversion in the reaction of isopropyl alcohol oxidation on binary molybdenum-vanadium oxide catalysts on the degree of surface acidity are shown in Fig. 5. It can be seen that as surface acidity increases (degree of isomerization of butene-1 to butenes-2) the acetone yield and total conversion of isopropyl alcohol increases as well, while the propylene yield practically does not change with

increasing surface acidity. This indicates that the increase in surface acidity expressed through the degree of isomerization of butene-1 to butenes-2 leads to the increase in the reaction rate of dehydrogenation of the initial alcohol into acetone. Based on the results obtained, it can be concluded that the reaction of oxidative dehydrogenation of isopropyl alcohol into acetone and propylene proceeds on acidic centers.

### Conclusion

The increase in surface acidity on binary molybdenum-vanadium oxide catalysts in the reaction of isopropyl alcohol dehydrogenation leads to the increase in acetone yield while the propylene yield passes through the maximum.

In the reaction of oxidative dehydrogenation of isopropyl alcohol, the increase in surface acidity leads to the increase in acetone yield while the propylene yield practically does not change.

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## ЗАВИСИМОСТЬ АКТИВНОСТИ БИНАРНЫХ Mo-V-O КАТАЛИЗАТОРОВ В РЕАКЦИЯХ ДЕГИДРИРОВАНИЯ И ОКИСЛЕНИЯ ИЗОПРОПИЛОВОГО СПИРТА ОТ КИСЛОТНЫХ СВОЙСТВ ПОВЕРХНОСТИ

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**Аннотация:** Изучена реакция дегидрирования и окислительного дегидрирования изопропилового спирта на молибден-ванадий оксидных катализаторах. Установлено, что зависимости конверсии изопропилового спирта и выходов пропилена в реакции дегидрирования изопропилового спирта от атомного отношения молибдена к ванадию имеют вид кривой с двумя максимумами на образцах Mo-V=2-8 и Mo-V=6-4. Для характеристики кислотных свойств поверхности молибден-ванадий оксидных катализаторов изучена также их активность в реакции изомеризации бутена-1 в бутены-2. Показано, что на молибден-ванадиевых катализаторах зависимость выходов бутенов-2 от соотношения молибдена к ванадию также имеет вид кривой с двумя максимумами. Сопоставлены активности молибден-ванадий оксидных катализаторов с их кислотными свойствами. Показано, что на бинарных молибден-ванадий оксидных катализаторах в реакции дегидрирования изопропилового спирта увеличение кислотности поверхности приводит к увеличению выхода ацетона и снижению выхода пропилена. В реакции же окислительного дегидрирования изопропилового спирта увеличение кислотности поверхности приводит к увеличению выхода ацетона, в то время как выход пропилена практически не меняется.

**Ключевые слова:** изопропиловый спирт, дегидрирование, окислительное дегидрирование, оксид ванадия, изомеризация, кислотность поверхности

## BİNAR Mo-V-O KATALİZATORLARININ AKTİVLİYİNİN İZOPROPİL SPİRTİNİN DEHİDROGENLƏŞMƏ VƏ OKSİDLƏŞMƏ REAKSİYALARINDA SƏTHİN TURŞU XASSƏLƏRİNDƏN ASILILIĞI

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**Xülasə:** İzopropil spirtinin molibden-vanadium oksid katalizatorlarında dehidrogenləşməsi və oksidləşməsi reaksiyaları tədqiq edilmişdir. Müəyyən edilmişdir ki, izopropil spirtinin dehidrogenləşmə reaksiyasında spirtin çevrilməsinin və propilenin çıxımının molibdenin vanadiuma atom nisbətindən asılılığı əyrisində Mo-V=2-8 və Mo-V=6-4 nisbətərində iki

maksimum müşhidə olunur. Molibden-vanadium oksid katalizatorlarının səthinin turşu xassələrini xarakterizə etmək üçün onların buten-1-in buten-2-yə izomerləşməsi reaksiyasında aktivliyi də öyrənilmişdir. Alınan nəticələrə əsasən göstərilmişdir ki, molibden vanadium katalizatorlarının iştirakı ilə buten-2-nin çıxımının molibdenin vanadiuma atom nisbətindən asılılığı əyrisində də iki maksimum var. Molibden-vanadium oksid katalizatorlarının aktivliyi onların turşu xassələri ilə müqayisə edilmişdir. Göstərilmişdir ki, ikili molibden-vanadium oksid katalizatorlarında izopropil spirtinin dehidrogenləşməsi reaksiyasında səth turşuluğunun artması asetonun çıxımının artmasına və propilenin çıxımının azalmasına səbəb olur. İzopropil spirtinin oksidləşdirici dehidrogenləşməsi reaksiyasında səth turşuluğunun artması asetonun çıxımının artmasına səbəb olur, propilenin şıxımı isə praktiki olaraq dəyişmir.

**Açar sözlər:** izopropil spirti, dehidrogenləşmə, oksidləşdirici dehidrogenləşmə, vanadium oksidi, izomerləşmə, səth turşuluğu.