# ABOUT THE NATURE OF THE ACTIVE CENTERS ON THE SURFACE MOLYBDEN-CONTAINING MULTICOMPONENT OXIDE THE CATALYST OF PROCESS AMMOXIDATION OF PROPENE

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*Surface reduction of complex molybden-containing oxide catalysts by the initial reactant in propene ammoxidation increases its activity in isomerization of butene-1 to butene-2. Isomerization and conversion of ammonia, propene and their mixtures are suggested to take place on the same active centers of the catalyst.*

In gas-phase heterogeneous oxidizing catalysis the condition of a surface of the firm catalyst plays an essential role at definition of a route of reaction, a degree of transformation of initial reagents and selectivity process. The acid centers of a superficial layer oxide catalysts participate mainly in reactions of soft oxidation whereas the basic centers are responsible mainly for deep oxidation [1].

In practice heterogeneous catalysis exist a beside of ways estimate acidities of a surface firm catalytic systems. Mainly these ways enable will define acidity in absence catalysis, that in turn does not give a real and high-grade picture of a superficial condition of the firm catalyst. Process isomerization butene-1 to butene-2 it has been offered as reaction of definition of sour properties of a contact surface oxide catalysts. The important advantage of a method - an opportunity of carrying out of research almost at catalytic conditions [2-4].

Attempt to investigate process isomerization butene-1 to butene-2 is undertaken at the presence of initial components of process ammoxidation of propene in conditions of reaction with the purpose of definition of the nature of the active centers of soft oxidation multicomponent molybden-containing oxide the catalyst.

## EXPERIMENTAL

Researches were carried out in microcatalytic to installation, with a reactor of the flowing type (v=3 $cm^3$ sample), a having stationary layer molibdenum-silicium-bismuth-phosphorum-oxide the catalyst. Volumetric speed of a stream $\tau$=400$h.^{-1}$ Structure multicomponent oxide the catalyst.

$$(MoO_3)_{48}\cdot(Bi_2O_3)_2\cdot(P_2O_5)\cdot(SiO_2)_{184}$$

Multicomponent contact system prepared a method joint from sedimentation using ammonium para-molybdate, nitrate of bismuth, orthophosphate for acids and silica sol. The evaporated paste of a deposit calcinated in current t = 1 h., at temperature T=940$^0$K. Investigated isomerization butene-1 to butene-2 at the presence of air, ammonia, propene and mixes propene-ammonia, and as in reactions of oxidation of ammonia, oxidations propene and ammoxidation of propene at the presence of air. Thus, a parity of initial components in a gas mix acting in a reactor remained constants.

butene-1 : air = 1 : 9
butene-1 : ammonia = 1 : 1
butene-1 : propene = 1 : 1
butene-1 : ammonia : propene = 1 : 1 : 1
butene-1 : ammonia : air = 1 : 1 : 8
butene-1 : propene : air = 1 : 1 : 8
butene-1 : ammonia : propene : air = 1 : 1 : 1 : 7

## RESULTS AND DISCUSSION

Preliminary researches have shown, that on molibdenum-silicium-bismuth-phosphorum-oxide the catalyst butene-1 - isomerized to the cis- and trans-butene-2 whereas skeletal isomerization does not take place. To characterize activity isomerization catalysts, by a degree of transformation butene-1 to the cis- and trans-butene-2 were used.

$$\alpha = \frac{\text{cis-butene-2}}{\text{tras-butene-2}}$$

In the temperature range examined the conversion degree of butene-1 to butene-2 on the samples pretreated with ammonia, propene and their mixtures was higher than on the oxidized samples (Fig.1).

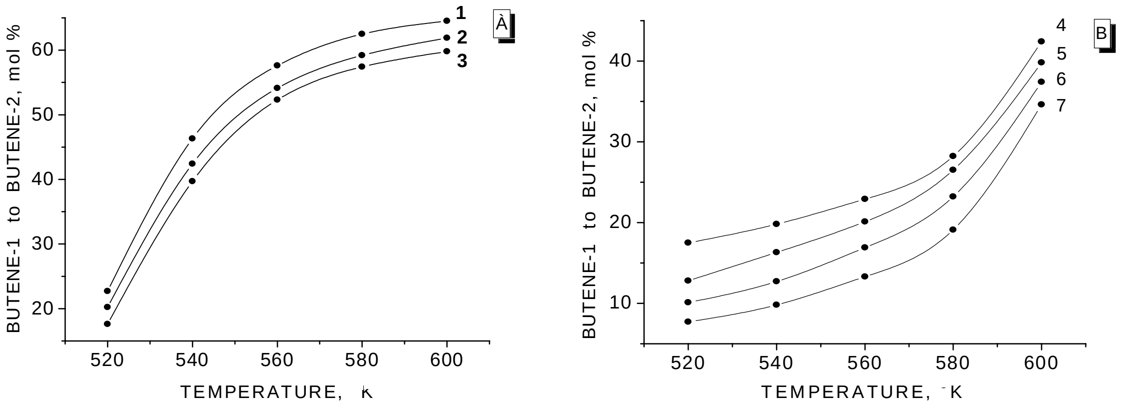

**Fig. 1.** Isomeization of butene-1 to butene-2 molibdenum-silicium-bismuth-phosphorum-oxide catalysts after treatment by different reaction components of the gas mixture for propene ammoxidation:
1 - ammonia; 2 - propene; 3 - ammonia and propene; 4 - air; 5 - propene and air; 6 - ammonia and air; 7 - ammonia, propene and air.

The enhancement of isomerization potential is, apparently, due to the catalyst reduction. Activation effect of oxygen vacancies in butene-1 isomerization has been shown previously by using bismuth molybdate [5].

One can also observe changes in the ratio of isomers, i.e. with increasing temperature the cis-isomer content on the oxidized surface increases faster than on the reduced samples. These data confirm the suggestion that basic centers ($0^{-2}$) promote the formation of cis-isomers, whereas asidic ones ($Me^{+n}$) are favorable for the formation of trans-isomers [6].

The results indicate that the nature of reductants does not exert any significant effect on the shape of the isomerization activity curve (Fig.1). A slight variation in the data obtained can be ascribed to surface carbonization and the formation of stable ammonia species. Catalyst activity is significantly affected by the reduction degree, which is primarily determined by the nature of catalyst and the reduction conditions.

As a result of ammonia and propene oxidation and ammoxidation on the catalyst, its surface is preserved in an almost oxidized state (Fig.1). Slightly decreased isomerization values compared to those obtained on the oxidized samples, can also be ascribed to surface carbonization and the formation of stable ammonia species.

Data on butene-1 isomerization upon introducing some components of propene ammoxidation are listed in Table 1.

When adding both butene-1 and propene to the reaction mixture, propene is not converted at temperature $T=580^0K$, whereas its conversion without butene-1 at the same temperature is 10 % [ 7 ].

It is likely that, under the conditions examined, there is a competitive adsorption of olefins with the predominance of butene-1. Therefore, data on the isomerization of buten-1 are close to the values obtained on the oxidized surfaces in the presence of air.

When the reaction mixture contains ammonia or both ammonia and propene, the isomerization data are similar. Thus, at temperature $T=580^0K$ the conversion of ammonia to molecular nitrogen is not higher than 10%, propene is not converted, and ammoxidation does not take place. Buten-1 isomerization is much weaker. Apparently, in this case the surface state of the catalyst changes considerably.

**Table 1. Isomerization of butene-1 to butene-2 ( mol % ) at temperature** $T=580^0K$

| Composition of initial gas mixture | Σ $C_4H_8$-2 | cis- $C_4H_8$-2 | tras- $C_4H_8$-2 | cis/tras $C_4H_8$-2 |
|---|---|---|---|---|
| $C_3H_6$:$C_4H_8$–1:air=1:1:8 | 23.9 | 12.7 | 11.2 | 1.13 |
| $C_4H_8$–1:air=1:9 | 24.9 | 13.1 | 11.8 | 1.11 |
| $NH_3$:$C_4H_8$–1:air=1:1:8 | 7.3 | 3.4 | 3.9 | 0.87 |
| $NH_3$:$C_3H_6$:$C_4H_8$–1:air=1:1:1:7 | 7.0 | 2.9 | 4.1 | 0.71 |

When adsorbed, ammonia neutralized the surface acidic centers, and when oxidized, it interacts with the surface basic centers. In this case the ratios of butene-2 isomers permit to suggest that isomerization mainly takes place during the competitive adsorption of ammonia and butene-1 on the centers reduced by ammonia.

## CONCLUSION

The results suggest that one of the main factors responsible for the high selectivity of molibdenum-silicium-bismuth-phosphorum-oxide catalysts in propene oxidation in presence of ammonia, is a definite sequence in the adsorption of reaction components. First of all ammonia is adsorbed and blocks acidic centers, then propene adsorption takes place.

The results also suggest that the isomerization of butene-1 to butene-2 and oxidative conversions of ammonia, propene and the their mixtures occur on the same active centers. This again confirms the validity of the evaluation of catalyst acidity according to its isomerization potential.

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## ***PROPENİN OKSİDLƏŞDİRİCİ AMMONOLİZ PROSESİNİN ÇOXKOMPONENTLİ MOLİBDEN-TƏRKİBLİ OKSİD KATALİZATORUNUN SƏTHİNDƏ MÖVCUD FƏAL MƏRKƏZLƏRİN TƏBİƏTİ HAQQINDA***

***Q.N. Hacıyev***

*Propenin oksidləşdirici ammonoliz prosesinin reaqentləri ihtirakında mürəkkəb molibden-tərkibli oksid katalizatorun səthinin reduksiyası buten-1 alkenin buten-2 izomerləşməsi prosesinin fəallığını yüksəldir. Tədqiqat nəticəsində əldə edilmiş dəlillərə əsasən ehtimal entmək olar ki, izomerləşmə, ammonyakın və propenin fərdi oksidləşmə və onların müştərək oksidləşmə reaksiyaları eyni fəal mərkəzlərdə həyata keçir.*

## ***О ПРИРОДЕ АКТИВНЫХ ЦЕНТРОВ НА ПОВЕРХНОСТИ МОЛИБДЕН-СОДЕРЖАЩЕГО МНОГОКОМПОНЕНТНОГО ОКСИДНОГО КАТАЛИЗАТОРА ПРОЦЕССА ОКИСЛИТЕЛЬНОГО АММОНОЛИЗА ПРОПЕНА***

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*Востановление поверхности сложного молибден-содержащего оксидного катализатора исходными компонентами реакции окислительного аммонолиза пропена приводит к повышению его активности в реакции изомеризации бутена-1 в бутен-2. Анализ полученных экспериментальных данных показывает, что реакции изомеризации, окисления аммиака, окисления пропена и их совместное окисление осуществляются на одних и тех же активных центрах.*