ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2016, Vol. 90, No. 6, pp. 1132–1136. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © I.I. Mishanin, A.N. Kalenchuk, K.I. Maslakov, V.V. Lunin, A.E. Koklin, E.D. Finashina, V.I. Bogdan, 2016, published in Zhurnal Fizicheskoi Khimii, 2016, Vol. 90, No. 6, pp. 855–859.

CHEMICAL KINETICS AND CATALYSIS

Deactivation of a Mixed Oxide Catalyst of Mo–V–Te–Nb–O Composition in the Reaction of Oxidative Ethane Dehydrogenation

I. I. Mishanin[a], A. N. Kalenchuk[a,b], K. I. Maslakov[a], V. V. Lunin[a,b], A. E. Koklin[b], E. D. Finashina[b], and V. I. Bogdan[a,b]

[a] *Department of Chemistry, Moscow State University, Moscow, 119991 Russia*

[b] *Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

e-mail: arnochem@yandex.ru

Received June 24, 2015

Abstract—The operational stability of a mixed oxide catalyst of Mo–V–Te–Nb–O composition in the oxidative dehydrogenation of ethane (ratio of $C_2H_6 : O_2 = 3 : 1$) is studied in a flow reactor at temperatures of 340–400°C, a pressure of 1 atm, and a WHSV of the feed mixture of 800 h^{-1}. It is found that the selectivity toward ethylene is 98% at 340°C, but the conversion of ethane at this temperature is only 6%; when the temperature is raised to 400°C, the conversion of ethane is increased to 37%, while the selectivity toward ethylene is reduced to 85%. Using physical and chemical means (XPS, SEM), it is found that the lack of oxidant in the reaction mixture leads to irreversible changes in the catalyst, i.e., reduced selectivity and activity. Raising the reaction temperature to 400°C allows the reduction of tellurium by ethane, from the +6 oxidation state to the zerovalent state, with its subsequent sublimation and the destruction of the catalytically active and selective phase; in its characteristics, the catalyst becomes similar to the Mo–V–Nb–O system containing no tellurium.

Keywords: oxidative dehydrogenation of ethane, mixed oxide catalyst, Mo–V–Te–Nb–O.

DOI: 10.1134/S0036024416060133

INTRODUCTION

Due to the growing demand for the deep, energy-efficient processing of natural, associated, and refinery gases, there is a strong need to develop processes for the dehydrogenation of such light hydrocarbons as ethane. One ways of solving this problem could be the oxidative dehydrogenation (OD) of lower alkanes, which has several advantages over direct dehydrogenation. First, OD is an exothermic process; this should certainly serve as an incentive to use it in the production of olefins. Second, the use of OD allows us to cope with the coking process, a cause of rapid catalyst deactivation.

There are currently a great many catalysts known for the oxidative dehydrogenation of ethane (ODE) [1]. It is known that the best results in ODE are shown by mixed oxide catalysts Mo–V–Te–Nb–O [2], which at a fairly low temperature (400°C) ensure 90% selectivity for ethylene at an ethane conversion of 60%. The activity of Mo–V–Te–Nb–O catalysts is largely determined by the ratio of metals in them, the temperature of treatment, the initial precursors for synthesis, and the methods of preparation [2–9].

The ODE reaction over the oxide catalysts proceeds according to the Mars–Van Krevelen step mechanism involving the alternating oxidation and reduction of the catalyst. One of the key elements responsible for the high selectivity toward ethylene in the ODE reaction is tellurium [5]. It is responsible for the formation of the highly selective orthorhombic M1 phase of the $Te_2M_{20}O_{57}$ composition (M = Mo, V, Nb) and prevents the formation of nonselective Mo- and V-containing crystalline phases [5].

The aim of this work was to study the stability of Mo–V–Te–Nb–O catalyst in the ODE reaction.

EXPERIMENTAL

Mixed oxide catalysts $Mo_{1.0}V_{0.37}Te_{0.17}Nb_{0.15}O_x$ (referred to below as Mo–V–Te–Nb–O) and $Mo_{1.0}V_{0.29}Nb_{0.15}O_x$ (below, Mo–V–Nb–O) were prepared via hydrothermal synthesis as described in [9]. The following substances were used as precursors: ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Acros Organics, 99+%), telluric acid $H_6TeO_6 \cdot 2H_2O$ (Alfa Aesar, 99+%), vanadyl sulfate $VOSO_4 \cdot xH_2O$ (Alfa Aesar, 99.9+%), and tris(oxalato)niobic acid $H_3[NbO(C_2O_4)_3] \cdot 7.5H_2O$ (Reakhim, special purity).

The crystallinity and phase composition of the fresh and spent catalysts were determined via X-ray diffraction on a DRON-2 unit (2θ range of 5° to 35°).

X-ray photoelectron spectra were recorded on a Kratos Axis Ultra DLD instrument using monochromatic AlK_α radiation (1486.6 eV). The pass energy of the analyzer was 160 eV for the survey spectra and 40 eV for the high resolution spectra. The spectra were recorded using a neutralizer. Energy calibration of the spectra was performed based on the position of Mo3$d_{5/2}$ line (233.2 eV).

Electron micrographs of the samples surfaces were obtained on a JEOL JSM-6390LA scanning electron microscope. The accelerating voltage (0.5 to 30 kV) was selected depending on the structure and material of a sample, as was the working distance (8–25 mm). Energy dispersive X-ray microanalysis spectra were recorded using EDS module at an accelerating voltage of 20 kV.

Our study of the catalytic oxidative dehydrogenation reaction was conducted using a flow unit (a titanium reactor with an inner diameter of 0.55 cm and a length of 58 cm) at atmospheric pressure in the temperature range of 340–400°C. To eliminate local overheating, the catalyst (in powder form) was mixed with titanium oxide TiO_2 at a ratio of 1 : 1 by weight. It was then compressed and a fraction of 0.25–0.5 mm was collected. The sample loading was 4 g. The mixture of $C_2H_6 : O_2 = 3 : 1$ was prepared in the gas cylinder by mixing ethane (purity, 99.9%) with technical oxygen (98%). The feed rate of the reaction mixture was 50 cm^3/min (space velocity, 800 h^{-1}).

The reaction products were analyzed by means of gas chromatography on an LKhM-80 chromatograph equipped with a thermal conductivity detector, using two packed columns (3 m × 0.3 mm) with different adsorbents: Porapak Q for analyzing hydrocarbons and carbon dioxide, and a CaA molecular sieve for analyzing oxygen, nitrogen, and carbon monoxide.

RESULTS AND DISCUSSION

Key findings from our study of three- and four-components oxide catalysts in the ODE reaction are shown in Table 1. The reaction products were ethylene, carbon oxides, and water. Trace amounts of acetic acid were detected. At 380°C, its content was hundredths of a percent.

Table 1. Oxidative dehydrogenation of ethane over Mo–V–Te–Nb–O and Mo–V–Nb–O catalysts

Catalyst	T, °C	Ethane conversion, wt %	Selectivity,%		
			C_2H_4	CO_2	CO
Mo–V–Te–Nb–O	340	6	98	2	0
	360	20	92	3	5
	380	34	88	3	9
	400	37	85	3	12
Mo–V–Nb–O	360	9	68	16	16
	400	21	70	9	21

It was found that raising the temperature of the reaction favored the complete oxidation of ethane to carbon oxides. According to our data, high selectivity toward ethylene (98%) was achieved on the Mo–V–Te–Nb–O catalyst at 340°C. The conversion of ethane rose to 30% when the temperature was raised from 340 to 400°C, but the selectivity toward the desired product (ethylene) was reduced to 85%. The slowing of conversion upon moving from 380 to 400°C was due to around 95% of the oxygen present in the mixture being consumed at 380°C, and complete conversion took place at 400°C. A further increase in temperature (above 400°C) in the presence of a $C_2H_6 : O_2 = 3 : 1$ mixture did not affect the conversion of ethane, which is limited by the amount of oxygen in the feed gas stream. An increase in the conversion of ethane would thus be possible if gas mixtures with large molar contents of oxygen were prepared, but such mixtures are explosive.

The sample containing no tellurium displayed not only low selectivity toward ethylene, but also exhibited lower (by nearly 50%) activity, confirming the key role of tellurium in the formation of the active and selective phase in the ODE reaction, the presence of which has been shown in studies of samples using X-ray diffraction (XRD).

Mo–V–Nb–Ta–O catalyst stability in ODE was studied by varying the reaction temperature. After exposing the sample at 360°C for 3 h, the temperature was raised to 400°C, kept there for 0.5 h, and returned to the initial temperature (360°C) (Fig. 1).

The studied catalyst operated stably at 360°C, and the conversion of ethane was 18%. After raising the temperature to 400°C, conversion was as high as 40%. After the reaction temperature was lowered from 400 to 360°C, however, the conversion of ethane fell by 50%, compared to the original value at the given temperature. The selectivity toward ethylene was also reduced. To find the reasons for the observed reduction in conversion and selectivity, the catalyst samples were studied via XRD, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM).

Analysis of literature data shows that the complex oxide Mo–V–Te–Nb–O systems contained M1 and M2 phases [10–12]. The XRD patterns of the catalysts used in this work are shown in Fig. 2. Three-component mixed oxides without tellurium form different phase compositions. The amount of the orthorhombic phase of M1 responsible for the selective ODE to ethylene was thus lower, affecting sample activity during the experiments described above.

To determine the stability of the studied Mo–V–Te–Nb–O catalysts, the samples were kept under high vacuum in the spectrometer chamber for 12 h. No changes in the composition of oxide systems following

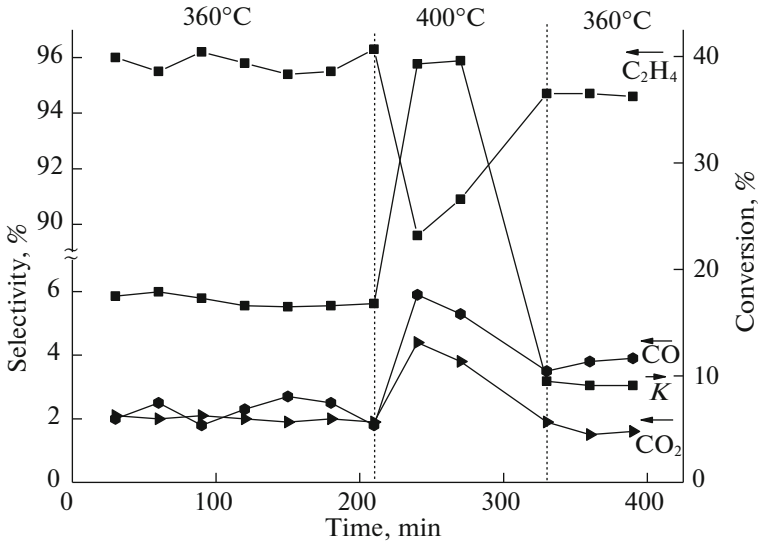

Fig. 1. Dependences of ethane conversion (*K*) and selectivity toward products in the reaction of OD in an oxygen–ethane mixture on time over the Mo–V–Te–Nb–O catalyst.

such exposure were noted by XPS data. The initial oxide systems and the samples pretreated in a stream of ethane and in a mixture of ethane and oxygen (in a ratio of 3 : 1) at a temperature of 400°C for 0.5 h were investigated via XPS. As was noted above, the oxygen of the gas phase was completely consumed at 400°C and there was a lack of oxidant in the system. The data for the Mo–V–Te–Nb–O sample treated with pure ethane thus represent the limiting case when there is absolutely no oxidant in the gas phase. The concentrations of elements on the catalyst's surface were calculated per 1 atom of molybdenum:

$$Mo_{1.00}V_{0.29}Nb_{0.24}Te_{0.32}O_{4.20}C_{0.51}\ \text{(initial)},$$

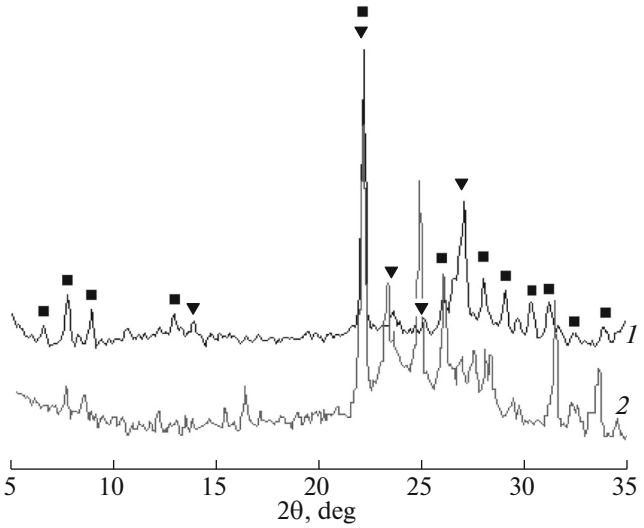

Fig. 2. XRD patterns of samples (*1*) Mo–V–Te–Nb–O, (*2*) Mo–V–Nb–O; (▼) phase M1, (■) phase M2.

$$Mo_{1.00}V_{0.27}Nb_{0.23}Te_{0.12}O_{3.88}C_{0.28}\ \text{(after } C_2H_6\text{)},$$

$$Mo_{1.00}V_{0.29}Nb_{0.24}Te_{0.36}O_{4.48}C_{0.24}\ \text{(after } C_2H_6/O_2\text{)}.$$

It follows from the gross formulas that after treatment with pure ethane, a strong reduction in the tellurium content was observed on the catalyst's surface. The concentrations of other metals vary slightly. There was a slight increase in the content of tellurium in the sample treated with a mixture of C_2H_6/O_2, due probably to redistribution of the element between the surface and the bulk phase. These changes in the concentration of tellurium are illustrated by Te3*d* XPS spectra in Fig. 3.

In addition to a substantial reduction in the signal intensity of tellurium at the higher Te^{+6} oxidation state, Te3$d_{5/2}$ state with an electron binding energy equal to 573.8 eV emerged in the spectrum of Te3*d* electrons after treating the sample with pure ethane. This binding energy is slightly higher than that of metallic tellurium (573.1 eV) and is characteristic of organotellurium compounds in which tellurium has a +2 oxidation state [13, 14]. In addition, it could be that tellurium surface structures have no direct analogy with the bulk phases.

Note that the observed reduction in the concentration of tellurium in the sample after the reaction could be due to the presence of reduced metallic tellurium on its surface that sublimates upon sample evacuation in the spectrometer chamber under ultrahigh vacuum. The spectra of the other metals (V, Nb, Mo) are virtually the same for all the samples.

Our results from X-ray microanalysis also confirmed the reduction of tellurium content in samples of the mixed oxide catalysts (Table 2).

Our study of mixed oxide systems via XPS and SEM showed that treating Mo–V–Te–Nb–O sam-

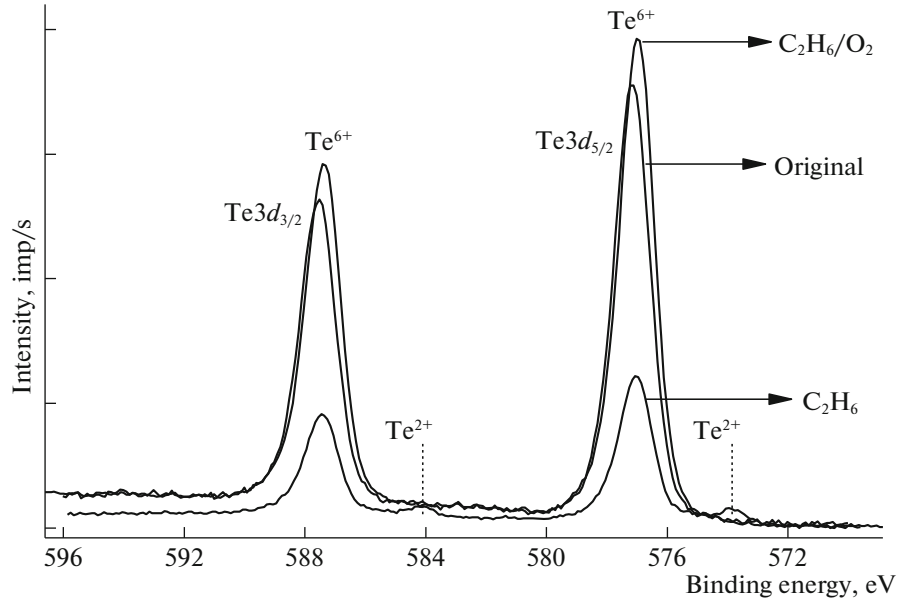

Fig. 3. Te3*d* XPS spectrum of the Mo–V–Te–Nb–O sample before and after treatment with C_2H_6 and C_2H_6/O_2.

ples in ethane with no oxygen varied their surface morphology considerably. The reduction of reactive tellurium species in the surface layer of the catalyst occurs as a result of its reduction with hydrocarbon with subsequent sublimation.

CONCLUSIONS

Under optimum reaction conditions (temperature, 360°C), the conversion of ethane on a four-component mixed oxide catalyst of Mo–V–Te–Nb–O is as high as 20% with a selectivity toward ethylene of 92%. Raising the reaction temperature to 400°C increases the total conversion of ethane with full engagement of the oxidant, but the selectivity toward ethylene is reduced to 85%. The catalyst is irreversibly deactivated under such operating conditions. It was shown that the reason for the observed catalyst deactivation was the partial reduction of tellurium to the metallic state, which proceeds in the reaction mixture with the complete consumption of the oxidizer. Catalyst deactivated in this manner exhibits lower conversion and selectivity toward ethylene in the ODE reaction that are similar to those obtained for a three-component oxide catalyst containing no tellurium.

Table 2. Concentrations of elements in catalyst Mo–V–Te–Nb–O before and after treatment with pure ethane, according to X-ray microanalysis

Element	Element fraction, wt %	
	before treatment	after treatment with ethane
O	13.75	13.05
V	8.96	9.16
Nb	10.20	9.85
Mo	55.04	57.47
Te	12.06	10.46

ACKNOWLEGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 13-03-12266-ofi_m; and by the ENVAIROKET Company. It was performed using equipment purchased under the Program for the Development of Moscow State University.

REFERENCES

1. F. Cavani, N. Ballarini, and A. Cericola, Catal. Today **127**, 113 (2007).
2. J. M. López-Nieto, P. Botella, P. Concepción, et al., Catal. Today **91–92**, 241 (2004).
3. P. Botella, J. M. López-Nieto, A. Dejoz, et al., Catal. Today **78**, 507 (2003).
4. K. Oshihara, Y. Nakamura, M. Sakuma, and W. Ueda, Catal. Today **71**, 153 (2001).
5. P. Beato, A. Blume, F. Girgsdies, et al., Appl. Catal. **307**, 137 (2006).
6. E. V. Ischenko, T. V. Andrushkevich, G. Ya. Popova, et al., in *Proceedings of the International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts, 2010,* p. 479.

7. T. T. Nguyen, M. Aouine, and J. M. M. Millet, Catal. Commun. **21**, 22 (2012).
8. B. Solsona, M. I. Vázquez, F. Ivars, et al., J. Catal. **252**, 271 (2007).
9. E. D. Finashina, A. V. Kucherov, and L. M. Kustov, Russ. J. Phys. Chem. A **87**, 1983 (2013).
10. H. Murayama, D. Vitry, W. Ueda, et al., Appl. Catal. **318**, 137 (2007).
11. P. Botella, J. M. López-Nieto, B. Solsona, et al., J. Catal. **209**, 445 (2002).
12. J. M. M. Millet, H. Roussel, A. Pigamo, et al., Appl. Catal. **232**, 77 (2002).
13. M. K. Bahl, R. L. Watson, and K. J. Irgolic, J. Chem. Phys. **66**, 5526 (1977).
14. M. R. Detty, W. C. Lenhart, P. G. Gassman, and M. R. Callstrom, Organometallics **8**, 861 (1989).

Translated by A. Pashigreva