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Oxidative Transformations of Ethane and Ethylene on VMoTeNbO Catalysts

V. M. Bondareva[a,*], **E. V. Lazareva**[a], **T. Yu. Kardash**[a,b], **and V. I. Sobolev**[a]

[a] Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
[b] Novosibirsk State University, Novosibirsk, 630090 Russia
*e-mail: valent@catalysis.ru

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Abstract—Comparative studies of oxidative transformations of ethane and ethylene were performed on multicomponent oxide catalysts of the preset cationic composition, $V_{0.3}Mo_1Te_{0.23}Nb_{0.12}$, differing in the final calcination temperature. The highest (~74%) ethylene yield in oxidative dehydrogenation of ethane is reached on the catalysts calcined in the temperature interval 550–650°C, which is due to the formation of the maximal amount of the active M1 phase.

Keywords: ethane, ethylene, oxidative dehydrogenation, VMoTeNbO catalysts

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Oxidative transformations of hydrocarbons of different classes, including selective oxidation and ammoxidation, are the basic processes in industrial production of such demanded monomers and products as acrylic acid, acrylonitrile, maleic and phthalic anhydrides, ethylene and propylene oxides, adipic and terephthalic acids, etc.

Oxidative dehydrogenation of ethane (ODE) attracts intent attention of researchers as an alternative to power-consuming pyrolytic processes for production of ethylene, the basic product of petroleum chemistry. The range of catalysts used for ODE is very wide, and multicomponent oxide formulations $Mo_1V_{0.2–0.4}Te_{0.20–0.25}Nb_{0.10–0.18}$ show the highest performance from the viewpoint of both the process conditions (temperature lower than 450°C, atmospheric pressure) and target product yield (70 ± 5%) [1–7]. The main crystalline phases in these catalysts are the so-called M1 and M2 phases of the composition $(Te_2O)M_{20}O_{57}$ and $(TeO)_xM_3O_9$ (M = Mo, Nb, V, $0 \leq x \leq 1$), respectively. High-temperature treatment ensuring the formation of the final chemical and phase composition of the catalysts is performed, as a rule, in an inert gas stream at 600°C. However, as shown in [8], the maximal conversion of ethane and the highest yield of ethylene in ODE are reached on the catalysts calcined at 650°C.

The major problem of heterogeneous oxidative catalysis as a whole and of the oxidative dehydrogenation in particular is the occurrence of side reactions of complete oxidation of both the initial substrate and the target product.

Here we report on a comparative study of oxidative transformations of ethane and ethylene under similar temperature and concentration conditions. Multicomponent oxides of the cationic composition $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$, calcined in the temperature interval 500–700°C, were used as catalysts.

EXPERIMENTAL

Catalyst preparation. Oxide catalysts of the preset cationic composition $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ were prepared by the procedure described in [9]. Ammonium paramolybdate $(NH_4)Mo_7O_{24}·4H_2O$ (Reakhim), ammonium metavanadate NH_4VO_3 (Reakhim), and telluric acid H_6TeO_6 (Aldrich) were dissolved in distilled water at 80°C with vigorous stirring. Niobium hydroxide was synthesized by precipitation of niobium pentachloride

($NbCl_5$, Acros Organics, 99.8%) with aqueous ammonia (25.5 wt %, Acros Organics) at pH 7 and was dissolved in an oxalic acid solution to obtain a solution of niobium oxalate ($C_2O_4^{2-}/Nb = 3.0$). This solution was added to the cooled mixed VMoTe solution. The gelatinous crude precursor formed was subjected to rapid drying with a laboratory drier (BÜCHI B-290, Germany). Then, the dry precursor was calcined for a short time in air at 300°C and then for 2 h in a helium stream in the temperature interval 500–700°C. The synthesized catalysts calcined at 500, 550, 600, 630, 650, and 700°C are denoted as A500, A550, A600, A630, A650, and A700, respectively.

A study of the physicochemical properties of the catalysts. The specific surface area of the synthesized catalysts was determined by the Brunauer–Emmett–Teller method from the isotherms of the low-temperature nitrogen adsorption with a DigiSorb-2600 installation (Micromeritics, the United States). Prior to sorption experiments, the samples were kept in a vacuum (10^{-4} mmHg) at 200°C for 5 h.

The chemical composition of the catalysts was determined with a Perkin Elmer ISP OPTIMA 4300DV atomic absorption spectrophotometer.

SEM images of catalyst samples were taken with a JSM 6460 LV scanning electron microscope (JEOL, Japan).

X-ray diffraction (XRD) analysis of the catalysts was performed with a Bruker D8 diffractometer using monochromated CuK_α radiation. Scanning was performed in the 2θ interval 5°–65° with a step of 0.05°; the accumulation time in each points was 3 s. Quantitative phase analysis by the Rietveld method was performed with the TOPAS v.4.2 program package using structural parameters from [10] and the ICSD database.

Catalytic tests. The catalytic properties of the synthesized samples were studied using a flow-through installation with on-line chromatographic analysis of the reaction mixture components. The experiments were performed at atmospheric pressure in a tubular reactor with the coaxially arranged thermocouple pocket in a fixed bed of the catalyst (particle size 0.25–0.50 mm) under the following conditions: temperature 400°C, feed composition ethane (ethylene) : oxygen : nitrogen = 10 : 10 : 80 (vol %). The contact time in the range 0.5–25 s was obtained by varying the amount of the catalyst loaded (1–20 cm^3) and the feed flow rate (3–20 L h^{-1}). Experiments with the empty reactor showed that the homogeneous oxidation did not occur under these conditions.

Physicochemical properties of MoVTeNbO catalysts

Sample	Chemical composition	S_{sp}, m^2 g^{-1}
A500	$V_{0.3}Mo_{1.0}Te_{0.18}Nb_{0.11}$	5.4
A550	$V_{0.3}Mo_{1.0}Te_{0.17}Nb_{0.11}$	6.2
A600	$V_{0.3}Mo_{1.0}Te_{0.17}Nb_{0.11}$	3.5
A630	$V_{0.3}Mo_{1.0}Te_{0.17}Nb_{0.12}$	2.8
A650	$V_{0.3}Mo_{1.0}Te_{0.16}Nb_{0.10}$	1.9
A700	$V_{0.3}Mo_{1.0}Te_{0.14}Nb_{0.11}$	1.0

In the course of the experiments, we determined the concentrations of the components of the feed and final mixture and calculated from the results obtained the conversion of the starting hydrocarbon X (%) and the selectivity with respect to reaction products S_i (%):

$$X = \frac{c_0 - c}{c_0} \times 100,$$

$$S_i = \frac{\frac{1}{n}c_i}{\sum_i \frac{1}{n}c_i} \times 100$$

where c_0 is the ethane (ethylene) concentration in the feed (M); c, ethane (ethylene) concentration in the final mixture (M); c_i, concentration of ith product in the final mixture (M); and n_i, stoichiometric coefficient.

The ethylene yield in ODE, Y (%), was calculated using the formula

$$Y = XS,$$

where X is the ethane conversion (%), and S, selectivity with respect to ethylene (fractions of unity).

To compare the catalyst activities, we calculated the rate of the overall ethane (ethylene) transformation at 10% conversion, W (mol m^{-2} h^{-1}), using the formula

$$W = \frac{(c_0 - c)U}{S_{sp}P},$$

where U is the feed flow rate (L h^{-1}); S_{sp}, specific surface area (m^2 g^{-1}); and P, catalyst weight (g).

The rate of the ethylene accumulation in the course of ODE, W_E (mol m^{-2} h^{-1}), was calculated using the formula

$$W_E = WS,$$

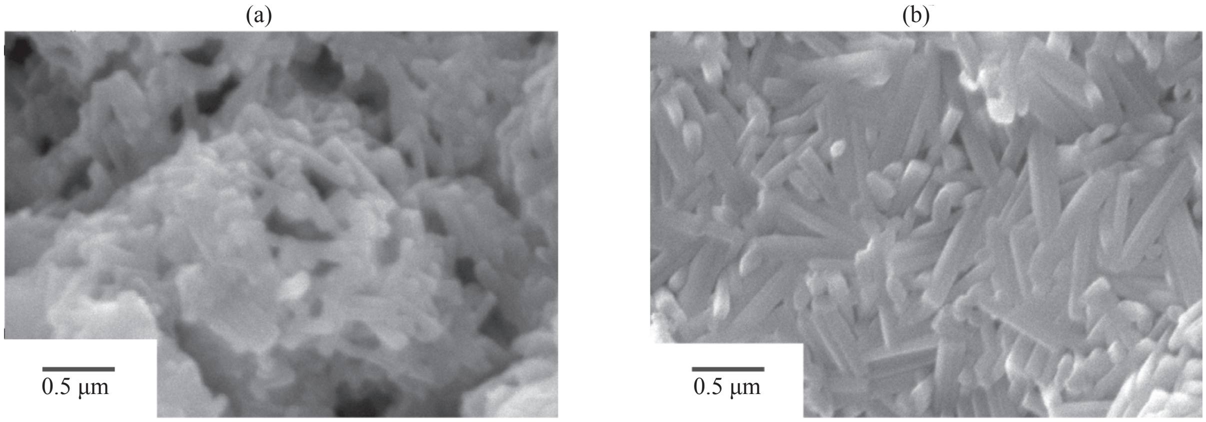


Fig. 1. SEM images of samples (a) A600 and (b) A700.

where W is the overall ethane transformation rate (mol m^{-2} h^{-1}), and S is the selectivity with respect to ethylene (fractions of unity).

RESULTS AND DISCUSSION

Physicochemical properties. The physicochemical characteristics of the synthesized catalysts are given in the table.

On the whole, the chemical composition of the catalysts corresponds to that set in the synthesis. The decreased tellurium content of the calcined samples is due to tellurium removal in the course of the high-temperature treatment as a result of partial reduction and formation of volatile Te^0 [11]. The specific surface area of the samples monotonically decreases with increasing calcination temperature over 550°C, which may be due to changes in the morphology of the synthesized catalysts.

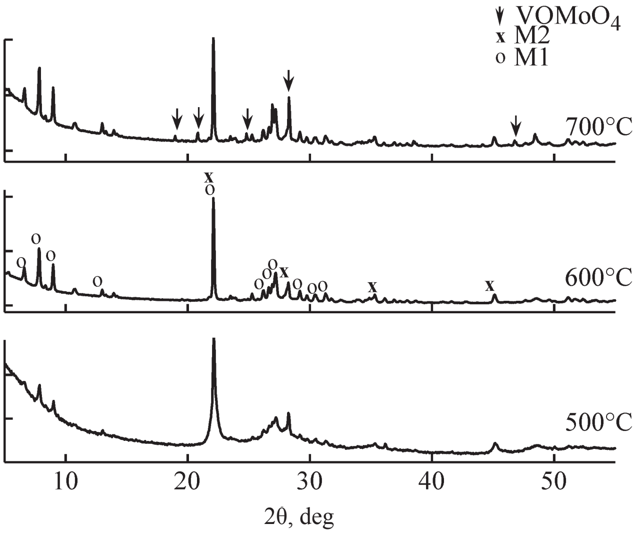


Fig. 2. X-ray patterns of samples calcined at 500, 600, and 700°C.

Figure 1 shows as example the SEM images of the samples calcined at 600 and 700°C. Indeed, an increase in the temperature leads to appreciable coarsening of crystallites and to a decrease in the porosity.

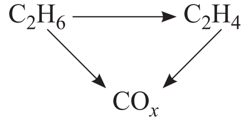
Figure 2 shows the X-ray diffraction patterns of the samples calcined in the temperature interval 500–700°C.

Sample A500 is poorly crystallized. The observed reflections correspond to those characteristic of the M1 (2θ = 6.6°, 7.9°, 9.0°, 22.1°, 27.2° [10]) and M2 (2θ = 22.1°, 28.2°, 36.1°, 45.1° [12]) phases. With an increase in the calcination temperature, the degree of crystallinity of these phases increases, as follows both from an increase in the reflection intensities and from the appearance of additional lines characteristic of the M1 and M2 phases. The X-ray diffraction patterns of the samples calcined in the interval 550–650°C are virtually identical and correspond to a mixture of the M1 and M2 phases. Further increase in the temperature to 700°C leads to the appearance of the $VOMoO_4$ phase, as indicated by the reflections appearing at 2θ = 19.9°, 20.8°, 24.8°, 28.4°, 44.2°, and 46.9° [8]. The M1 phase is the major phase in all the synthesized catalysts, and the calcination temperature influences its crystallinity and content. As shown previously [13], specifically the

M1 phase in VMoTeNbO catalysts is responsible for their activity in oxidative dehydrogenation of ethane.

Catalytic properties. The major ODE product is ethylene, with carbon oxides formed as by-products.

Figure 3 shows for sample A550 as example how the selectivity with respect to ODE products depends on the ethane conversion. Similar dependences were obtained for all the catalysts synthesized. The observed selectivity trends allow the oxidative conversion of ethane to be described by the scheme of consecutive-parallel reactions



According to this description, at low conversions of the starting compound carbon oxides are formed via the parallel pathway. With an increase in the conversion, the contribution of the consecutive pathway increases, and at high conversions, extremely important for industrial processes, carbon oxides are mainly formed by further oxidation of the selective reaction product.

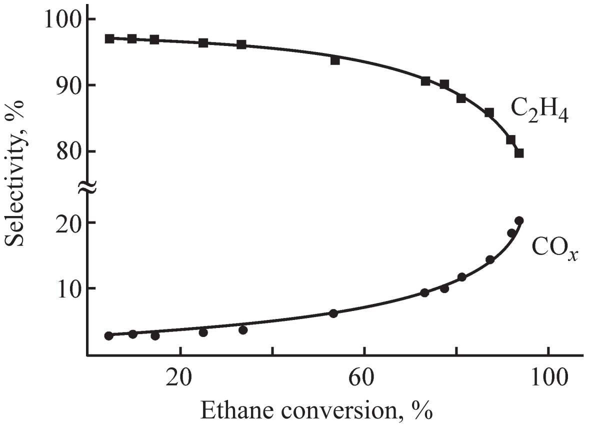


Fig. 3. Selectivity with respect to reaction products as a function of the ethane conversion on the MoVTeNbO catalyst calcined at 550°C.

Figure 4 shows how the selectivity with respect to ODE products at the ethane conversion of 10 and 80% depends on the catalyst calcination temperature. The dependences of the selectivity with respect to carbon oxides and ethylene are described by curves with a broad extremum (minimum for CO_x and maximum for C_2H_4) in the temperature interval from 550 to 650°C. The influence of the catalyst calcination temperature on the distribution of the reaction products is manifested more strongly at high ethane conversion, i.e., in the region where the consecutive pathway, further oxidation of ethylene, prevails.

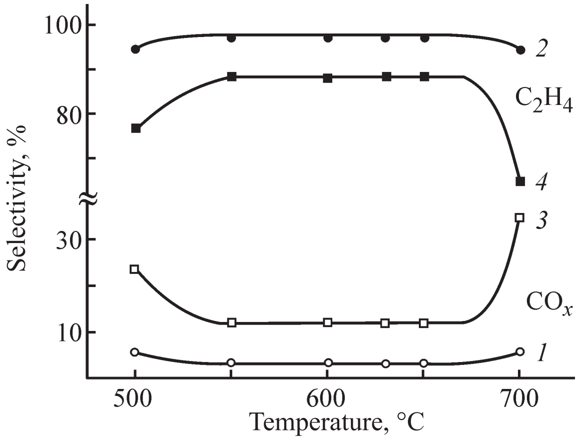


Fig. 4. Selectivity with respect to ethylene and to carbon oxides at (*1*, *2*) 10 and (*3*, *4*) 80% conversion of ethane as a function of the catalyst calcination temperature.

The products of the ethylene oxidation under the conditions of our experiments (400°C, ethylene : oxygen = 1 : 1) are carbon oxides. The CO/CO_2 ratio is close to 3 and varies only slightly in the examined interval of ethylene conversions (2–40%) for all the catalysts synthesized.

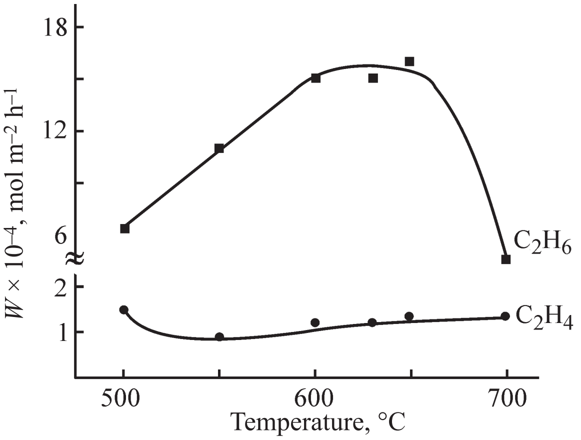


Fig. 5. Overall ethane and ethylene transformation rates as functions of the catalyst calcination temperature.

Figure 5 shows the plots for the overall ethane and ethylene transformation rates at 10% conversion, reflecting the influence of the calcination temperature on the catalyst activity in oxidative dehydrogenation of ethane and oxidation of ethylene. All the synthesized catalysts are more active in oxidative dehydrogenation of ethane than in deep oxidation of ethylene. However, the calcination temperature influences the catalyst

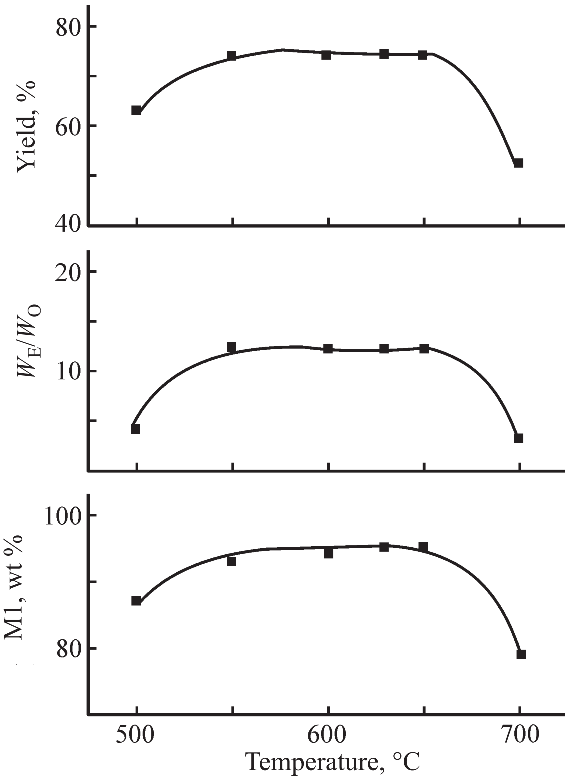


Fig. 6. Influence of the calcination temperature on the phase composition and catalytic performance of the catalysts.

activity in these reactions differently. For example, as the temperature is increased from 500 to 550°C, the overall ethane and ethylene transformation rates change in the opposite directions, increasing and decreasing, respectively. As the catalyst calcination temperature is increased further to 650°C, the rate of both reactions increased, especially in going from 550 to 600°C. Calcination at 700°C leads to a drastic decrease in the overall ethane transformation rate but does not affect the ethylene transformation rate.

Figure 6 shows the influence of temperature on the phase composition and catalytic properties of the VMoTeNbO catalysts. The content of the catalytically active M1 phase, ratio of the ethylene accumulation and oxidation rates (W_E/W_O), and ethylene yield (at 90% ethane conversion) are plotted. All these characteristics demonstrate similar trends and are described by curves with broad maxima. Similar curves (with flat extremum) describe the influence of the catalyst calcination temperature on the selectivity with respect to ODE products (Fig. 4).

Heat treatment of the catalyst at 550–650°C ensures constant and high content of the M1 phase (92–95 wt %). A characteristic feature of this phase is significant prevalence of the ethylene formation over its oxidation. This fact causes high values of the ethylene formation selectivity and yield. The constancy of the phase composition and catalytic properties at the calcination temperature varied in a wide interval shows that the M1 phase synthesized by the above-described procedure exhibits high thermal stability. This fact is extremely important, because, in accordance with the published data [14–17], VMoTeNbO catalysts are very sensitive to the methods and conditions of their synthesis.

The calcination temperature of 500°C is insufficient for the formation of the well crystallized M1 phase. At temperatures higher than 650°C, the $VOMoO_4$ phase is formed. Its content in sample A700 is 20 wt %. In both cases, the ratio of the ethylene formation and oxidation rates decreases, leading to a decrease in the ethylene yield.

CONCLUSIONS

A comparative study of the oxidative transformations of ethane and ethylene on multicomponent oxides of the cationic composition $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$, calcined in the temperature interval 500–700°C, was performed. At 400°C in the reaction mixture with the hydrocarbon : oxygen ratio of 1 : 1, all the synthesized catalysts are more active in oxidative dehydrogenation of ethane than in oxidation of ethylene.

The catalyst calcination temperature determining the qualitative and quantitative phase composition influences the ratio of the overall ethane and ethylene transformation rates. The maximal yield of ethylene in oxidative dehydrogenation of ethane is reached on the catalysts calcined at 550–650°C owing to the highest content of the active M1 phase in such catalysts.

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