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Advantages of ethane oxidative dehydrogenation on the MoVNbTeO$_x$ catalyst under elevated pressure

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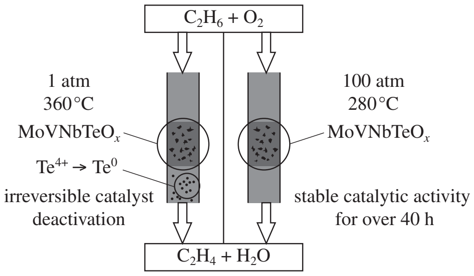
The oxidative dehydrogenation of ethane in the supercritical state into ethylene on MoVNbTeO$_x$ oxide catalysts at the total pressure of an O$_2$-containing mixture of 100 atm was carried out. The high reaction pressure allowed us to decrease the temperature from 360 °C at 1 atm to 280 °C at 100 atm along with the increased productivity of C$_2$H$_4$ from 205 to 290 $g_{C_2H_4}$ h^{-1} kg_{cat}^{-1}, respectively. Moreover, the higher pressure also prevents the destruction of M1 phase of the catalyst *via* the reduction of Te.



Along with the increasing demand of polymer industry for monomers, there is a growing need to develop efficient processes for the conversion of light hydrocarbons into olefines. In particular, the oxidative dehydrogenation of ethane (ODE) is among the most promising options for the production of ethylene since it provides a number of advantages in comparison with the traditional pyrolysis technologies. First of all, it allows one to avoid an equilibrium limitation of the hydrocarbon conversion due to the inclusion of a number of reactions. Secondly, ODE is an exothermic process releasing the energy in contrast to the endothermic direct dehydrogenation. Last but not least, such a dehydrogenation with the involved oxidizer makes it possible to reactivate the catalyst *in situ*.

Either O$_2$ or CO$_2$ can be employed as the oxidizing agent in the ODE process. In the case of CO$_2$, ODE proceeds with noticeable conversions at the temperatures above 600 °C, systems based on Fe, Ga, Ni and Cr oxides deposited on SiO$_2$, Al$_2$O$_3$, MCM-41 and MgO being used as the catalysts. Major problems include the low selectivity and carbonization of the catalyst surface.[1]

In the case of O$_2$, the best results were observed for catalysts based on MoVO$_x$ doped with various metal additives (Te, Nb, or Sb).[2–15] The MoVTeNbO$_x$ catalysts are most promising for this process. Many variations in the catalyst synthesis parameters and process itself were employed in order to improve characteristics of this process (C$_2$H$_6$ conversion, selectivity towards ethylene, and catalyst lifetime). For instance, an efficient ODE process with a selectivity of 90% or above with respect to C$_2$H$_4$ was developed at the C$_2$H$_6$ conversion of 80%.[3] The optimal activation parameters for the ODE catalyst were achieved by its calcination at 600 °C under a stream of Ar.[4,5] A synthesis technique for the active catalysts with a final suspension at pH 3 was also developed.[8] However, there is only one report[12] on the effect of low pressure on the activity and selectivity of the MoVTeNbO$_x$ catalyst in ODE. The experiments were carried out at 400 °C and pressures of 1–20 atm using the C$_2$H$_6$–O$_2$–N$_2$ mixture in a 15 : 18 : 67 (v/v) ratio. It has been found that the increased pressure favors a significant increase in the C$_2$H$_6$ conversion: from 25% at 1 atm up to 90% at 20 atm. However, the fraction of products of the complete C$_2$H$_6$ oxidation increases in this case, while the C$_2$H$_4$ selectivity decreases from 97 to 75%, respectively. Note that no attention was paid to the problem of MoVTeNbO$_x$ catalyst deactivation that is irreversible in the temperature range of 360–400 °C, which was shown in our previous work.[13]

Thus, the present work was aimed at the establishment of kinetic characteristics for the ODE process in supercritical state and at the determination of effect of these reaction conditions on the irreversible deactivation of the mixed oxide catalyst, MoVNbTeO$_x$.

Catalysts with the composition of Mo$_{1.0}$V$_{0.37}$Te$_{0.17}$Nb$_{0.15}$O$_x$ (hereinafter mentioned as MoVNbTeO$_x$) were prepared *via* a hydrothermal synthesis.[†] The ODE process was carried out in

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[†] Ammonium heptamolybdate tetrahydrate (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Acros Organics, 99+%), telluric acid H$_6$TeO$_6$·2H$_2$O (AlfaAesar, 99+%), vanadyl sulfate VOSO$_4$·xH$_2$O (AlfaAesar, 99.9+%) and niobium oxalate in its ammonium form (HCStarck, 20.7% Nb, 53.64%, C$_2$O$_4$, 5.13% NH$_3$) were used as received. Catalysts (composition of Mo$_{1.0}$V$_{0.37}$Te$_{0.17}$Nb$_{0.15}$O$_x$) were prepared *via* hydrothermal synthesis according to the known procedure.[2] (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (26.50 g) and H$_6$TeO$_6$·2H$_2$O (5.75 g) were dissolved in distilled water (19.5 g) at 80 °C. An aqueous solution of ammonium hydroxide (25%) was added dropwise to this solution until pH 7.5. Water was evaporated under continuous stirring at 80 °C. The solid residue was dried at 90 °C. The resulting white powder of ammonium molybdotellurate (6.4 g) was resuspended in H$_2$O (21.3 g) at 80 °C. A solution of VOSO$_4$·xH$_2$O (2.39 g) in H$_2$O (10 ml) was added to the suspension, followed by the addition of solution of niobium oxalate (2.33 g) in H$_2$O (10 ml). The resulting mixture was stirred for 10 min and transferred into a stainless steel autoclave equipped with an internal Teflon® cup. The autoclave was purged with an inert gas, sealed, and heated to 175 °C. The system was held at this temperature for 48 h. The autoclave was then cooled to room temperature, and the solid precipitate formed after the hydrothermal synthesis was filtered, washed with distilled water until the rinse water lost its color, and dried at 80 °C. The resulting precursor

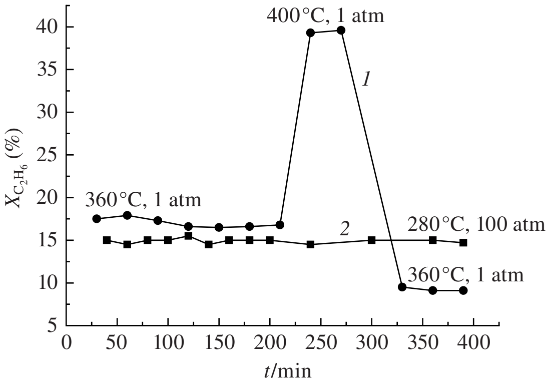

Figure 1 Dependences of C_2H_6 conversion in the ODE reaction on the experiment time: (*1*) $P = 1$ atm, $T = 360$ or 400 °C, $C_2H_6 : O_2 = 75 : 25$ (v/v), $v = 1500\ h^{-1}$ and (*2*) $P = 100$ atm, $T = 280$ °C, $C_2H_6 : O_2 : N_2 = 31 : 23 : 46$ (v/v), $v = 2400\ h^{-1}$.

a flow-through unit.[‡] The $C_2H_6–O_2–N_2$ gas mixture in a ratio of 31 : 23 : 46 (v/v) at the inlet was fed into the reactor.[§] Technically, it is unsafe to work with mixtures of C_2H_6 possessing the highest explosive limit of 66% and pure oxygen under atmospheric and, especially, elevated pressures. Therefore, ODE was performed using mixtures, wherein the volume content of O_2 did not exceed 30%, or mixtures diluted in half with N_2. Two mixtures were selected in order to estimate the effect of dilution of the initial mixture on the ethylene productivity under atmospheric pressure: $C_2H_6 : O_2 = 75 : 25$ (v/v) (without dilution) and $C_2H_6 : O_2 : N_2 = 31 : 23 : 46$ (v/v) (diluted with N_2).

It was reported earlier[13] and confirmed in this work that a significant (more than 10%) conversion of C_2H_6 into C_2H_4 for an O_2-containing mixture under atmospheric pressure occurred at temperatures above 360 °C. Figure 1 shows the dependence of C_2H_6 conversion on the experiment time for the ODE process performed at 1 and 100 atm.

According to previous experimental XPS data,[13] a gradual irreversible deactivation of the MoVNbTeO$_x$ catalyst occurs under atmospheric pressure even at 360 °C during a long-term operation. Since this process is accelerated upon rising reaction temperature, a cyclic experiment was conducted. As the temperature increases from 360 to 400 °C, the C_2H_6 conversion grows from 17 to 37%. Upon returning to the reaction temperature of 360 °C, the C_2H_6 conversion decreased twofold down to 8%. As we have shown,[13] a complete consumption of O_2 from the reaction mixture in the ODE reaction results in the irreversible deactivation of MoVNbTeO$_x$ catalyst due to the reduction of tellurium of active phase M1 by C_2H_6. Carrying out ODE under elevated pressure prolongates the stable operation of MoVNbTeO$_x$ catalyst. The long-term (for 40 h) catalyst operation in this reaction at 100 atm and 280 °C proceeds with a high selectivity, while the C_2H_6 conversion into C_2H_4 is 15%.

Table 1 Oxidative C_2H_6 dehydrogenation by O_2-containing mixtures on the MoVTeNbO$_x$ catalyst at 1 and 100 atm.

P/atm	*T*/°C	$X_{C_2H_6}$ (%)	X_{O_2} (%)	Selectivity (%)					Productivity for C_2H_4/ g h^{-1} kg$^{-1}_{cat}$
				C_2H_4	CO_2	CO	CH_4	H_2	
1[a]	280	1	2	100	0	0	0	0	12
	340	6	10	98	2	0	0	0	72
	360	17	60	92	4	4	0	0	205
	400	37	100	85	4	11	0	0	412
1[b]	280	2	3	100	0	0	0	0	11
	340	8	11	97	3	0	0	0	42
	360	23	37	90	4	6	0	0	112
100[c]	240	2	3	91	9	0	0	0	40
	260	6	9	87	13	0	0	0	108
	280	15	24	88	12	0	0	0	288
	400	81	100	0	9	41	44	6	0

[a] $P = 1$ atm, $C_2H_6 : O_2 = 75 : 25$ (v/v), $v = 1500\ h^{-1}$. [b] $P = 1$ atm, $C_2H_6 : O_2 : N =$ $= 31 : 23 : 46$ (v/v), $v = 1500\ h^{-1}$. [c] $P = 100$ atm, $C_2H_6 : O_2 : N_2 = 31 : 23 : 46$ (v/v), $v = 2400\ h^{-1}$.

Table 1 summarizes the acquired results for the ODE process under atmospheric and elevated pressures on the MoVNbTeO$_x$ catalyst.

Acording to Table 1, for the mixture $C_2H_6 : O_2 = 75 : 25$ (v/v), the ODE process at 1 atm was initiated at 280 °C, but the C_2H_6 conversion did not exceed 1%. Upon higher temperature, it increased significantly thus reaching 17% at 360 °C. The C_2H_4 productivity was enhanced from 12 to 205 g h^{-1} kg$^{-1}_{cat}$ in this case. Note that the O_2 conversion was 60% already at 360 °C. In the case of diluted mixture $C_2H_6 : O_2 : N_2 = 31 : 23 : 46$ (v/v), the C_2H_6 conversion was improved by few percents, however the performance with respect to C_2H_4 was significantly reduced. Conducting the ODE process under the total pressure of 100 atm allows one to decrease the reaction temperature from 360 to 280 °C and, at the same time, to increase C_2H_4 productivity up to 290 g h^{-1} kg$^{-1}_{cat}$. In this case, the O_2 consumption does not exceed 25%, which agrees with the reaction stoichiometry taking into account the C_2H_6 conversion and selectivity towards C_2H_4.

Increasing the ODE temperature up to 400 °C under atmospheric pressure makes it possible to achieve the ethylene productivity of 412 g h^{-1} kg$^{-1}_{cat}$, however, as noted above, the catalyst would be irreversibly deactivated under these conditions. If the reaction is carried out at 100 atm and 400 °C, the ODE into ethylene would not proceed. Though complete consumption of oxygen occurs, a considerable fraction of ethane is converted into CH_4 and H_2. The main direction of C_2H_6 conversion involves its deep oxidation into carbon oxides and H_2O.

Thermodynamical analysis of the ODE and topochemical reactions occurring on the catalyst revealed the parameters for achieving a high efficiency of the ODE process by lowering the reaction temperature and increasing the pressure.

Deactivation of the catalyst is caused by the destruction of formed active phase M1. Under the ODE reaction conditions,

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was annealed for 2 h under inert gas flow at 600 °C (heating rate of 1.67 K min^{-1}). The obtained powder was pelleted, grounded, and sieved yielding the fraction containing particles of the required size.

[‡] The ODE process was performed in a flow-through unit at pressures of 1 and 100 atm in the temperature range of 240–400 °C. The catalyst (1–2 g, bulk density of 1.33 g cm^{-3}, fractions of 0.25 to 0.5 mm) was loaded into a steel reactor containing the immobilized catalyst layer located in the center, while the rest of reactor was filled with quartz sand. The reagents were fed into this system using liquid pumps. Since mixtures of C_2H_6 with O_2 are explosive under certain conditions, N_2O was employed as the source of O_2 in the operations under pressure. Nitrous oxide was decomposed directly during the reaction, prior to the reactant mixing unit, on HZSM-5 hydroxylated catalyst at 450 °C.

[§] The composition of reaction products was analyzed by gas chromatography using an LKhM-80 instrument equipped with a catharometer and two packed columns: Porapack Q (1.5 m) for the analysis of hydrocarbons and CO_2 and Zeolite A for the analysis of O_2 and CO.

The conversion of ethane and selectivity towards the product formation (ethylene and carbon oxides) were calculated using the following equations: $X_{C_2H_6} = [(C^0_{C_2H_6} - C_{C_2H_6})/C^0_{C_2H_6}] \times 100$, where $X_{C_2H_6}$ (%) is the ethane conversion, $C^0_{C_2H_6}$ is the initial ethane concentration, and $C_{C_2H_6}$ is the ethane concentration after the reaction; $S(P_i) = \{[C(P_i)/\nu_i]/[C^0_{C_2H_6} - C_{C_2H_6}]\} \times 100$, where $S(P_i)$ (%) is the selectivity towards product P_i, $C(P_i)$ is the concentration of product P_i after the reaction, and ν_i is the stoichiometric coefficient of product P_i.

The phase composition of the initial and used catalysts was determined using X-ray powder diffraction analysis performed on a DRON-2 instrument (the sample weight was 80 mg, 2θ varied from 10 to 50°).

tellurium ions are reduced by the hydrocarbon under oxidant deficiency conditions according to the following reaction:

$$TeO_2(s) + 2C_2H_6(g) = Te(s) + 2H_2O(g) + 2C_2H_4(g), \quad \Delta H = +112 \text{ kJ mol}^{-1}. \qquad (1)$$

Since the volume increases in this process, an increase in the total system pressure favors a shift of the equilibrium in reaction (1) to the left. Decreasing the ODE temperature also keeps the catalyst active phase intact. On the other hand, as the pressure grows, the surface concentrations of reagents increase along with selective activation of O_2 occurring *via* a dissolution in the bulk oxide phase, which significantly accelerates the process. This, in turn, allows one to reduce the ODE temperature and avoid the formation of complete C_2H_6 oxidation products.

The catalytically active phase for the selective C_2H_4 production from C_2H_6 is the M1 phase.[3] In this phase, the molybdenum and vanadium ions are located in the centers of octahedra articulated with each other forming hexagonal, heptagonal and pentagonal channels. Niobium cations are localized in pentagonal channels, where Mo and V ions are present in smaller amounts. Tellurium ions are located in the hexagonal and heptagonal channels. It is known[15] that the selective C_2H_6 dehydrogenation occurs inside the heptagonal channels of Mo_3VO_x and $MoVNbTeO_x$ catalysts. In the case of Mo_3VO_x, the catalytic system without niobium and tellurium, the heptagonal channels are unoccupied, and the catalyst exhibits a high activity along with low selectivity towards C_2H_4. At the same time, they are partially occupied with tellurium ions in mixed oxide systems $MoVTeNbO_x$. Due to the presence of tellurium ions in the catalyst, it is possible to achieve the high selectivity towards C_2H_4.

Figure 2 shows X-ray powder diffraction data of the initial sample and catalysts exposed for 6 h to the ODE reaction at 100 atm and temperatures of 280 and 400 °C.

It was found that the phase composition of samples before and after the reaction performed at 280 °C and 100 atm were almost identical. At the same time, a sharp decrease in the intensity of reflections at $2\theta = 22.18$, 27.18 and 45.18° characteristic of the M1 active phase was observed in the XRD spectra of catalyst recorded after the reaction at 400 °C. The formation of an X-ray amorphous phase during the ODE process on the catalyst under these drastic conditions indicates that the irreversible destruction of the active oxide phase occurs. A similar phenomenon of catalytically active phase destruction was also observed in the case of the catalyst operation in an oxygen-containing mixture under atmospheric pressure and at temperatures above 360 °C.[13] The reason for the deactivation of $MoVNbTeO_x$ catalyst was found using XPS analysis (Figure 3).

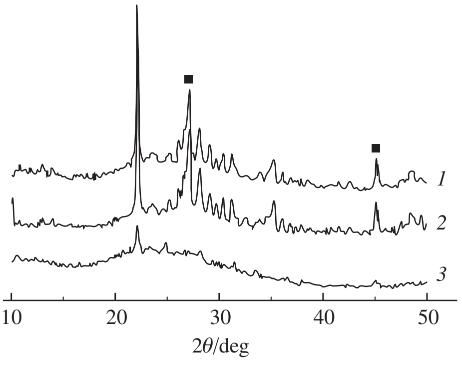

Figure 2 Diffractograms of the $MoVNbTeO_x$ catalyst (■ – M1 phase): (*1*) starting sample; and that after the reaction: (*2*) at 280 °C and 100 atm, (*3*) at 400 °C and 100 atm ($C_2H_6 : O_2 = 3:2$, $v = 2400$ h^{-1}, 6 h).

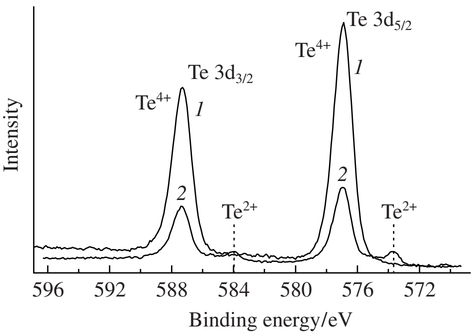

Figure 3 XPS spectra of the $MoVTeNbO_x$ catalysts (*1*) before and (*2*) after the reaction at 400 °C with mixture $C_2H_6 : O_2 = 3:1$ (v/v).

It was revealed that during the reaction at temperatures above 360 °C, C_2H_6 reduces tellurium from Te^{4+} to its zero-valent state Te^0 followed by the sublimation of metallic tellurium on the surface of quartz reactor. Ultimately, the irreversible decomposition of active phase of the $MoVNbTeO_x$ catalyst occurred.

In conclusion, we have demonstrated that the increase in the reaction pressure from 1 atm at 360 °C to 100 atm leads to an essentially decreased temperature (280 °C) of the ODE process performed on the $MoVNbTeO_x$ catalyst, while the selectivity towards C_2H_4 is maintained above 90% without any significant destruction of M1 phase *via* the reduction of Te. At the same time, the C_2H_4 productivity has been improved from 205 to 290 $g_{C_2H_4}$ h^{-1} kg$^{-1}_{cat}$.

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