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Effect of feedstock impurities on activity and selectivity of V-Mo-Nb-Te-O_x catalyst in ethane oxidative dehydrogenation

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Abstract:
The effect of CH_4, C_2H_4, CO_2, CH_3OH, and $(CH_3S)_2$ on activity and selectivity of V-Mo-Nb-Te-O_x catalyst for ethane oxidative dehydrogenation is studied. Methane acts as a chemically inert diluent of the gas mixture. Presence of ethylene in feed stream does not have significant effect on the rate of ethane dehydrogenation but causes slight drop in ethylene selectivity. CO_2 added is not involved in chemical transformations but suppress slightly ethane conversion and selectivity. Contamination of the gas stream with small amounts of either methanol or dimethyldisulfide (DMDS) does not reduce either activity or selectivity of the catalyst in ethane oxidative dehydrogenation.

Keywords: ethane, oxidative dehydrogenation, impurities, mixed oxide catalyst

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Introduction

The method of selective oxidative dehydrogenation (SOD) of ethane, although thermodynamically very favorable, suffers in practical application from unsatisfactory selectivity and activity of the existing catalysts/processes. The quaternary V-Mo-Nb-Te-O_x catalytic system being widely studied in propane oxidation/ammoxidation [1–7] seems to be the most promising also for ethane SOD. V-Mo-Nb-Te-O_x catalysts exceed noticeably other mixed oxides, such as NiO/MgO [8], Cr-V-O [9] or $CeVO_4$ [10], in both activity and selectivity of ethane SOD. The orthorhombic M_1-phase ($Te_2M_{20}O_{57}$; M = Mo, V, and Nb) seems to play a key role in activation of ethane [11–14], propane [15–17] and butane [18] upon different alkanes SOD on V-Mo-Nb-Te-O_x. Mixed oxides under study represent hybrid materials, which are known to be promising for many applications [19].

From the commercial operation point of view, to be competitive with classical steam cracking, ethane SOD would require higher ethane conversions and ethylene selectivities. One potential option for process improvement would be recycling mode operations. Under these conditions ethylene content in the product stream should increase, while unreacted oxygen decrease. However, several important questions could be immediately raised, e. g. what would be the impact of the presence of reaction products (ethylene, CO_2), or impurities on ethane SOD [20, 21]. This paper aims the comparison of ethane SOD, on V-Mo-Nb-Te-O_x containing the active orthorhombic M1-phase catalyst, in the absence and presence of either reaction products (C_2H_4, CO_2), or additives such as CH_4, CH_3OH, and DMDS. These last represent typical impurities of ethane feedstock extracted from natural gas, or ethane that is recycled in steam cracking plants.

It was shown earlier [11, 12, 23] that the quaternary V-Mo-Nb-Te-O_x catalysts demonstrated high activity and selectivity in low-temperature SOD of pure ethane exceeding dramatically those of three- and two-component mixed oxides. So, one of the goals of our study is to check the possibility of catalytic treatment of row initial mixture without preliminary deep purification using such quaternary catalyst. On the other hand, study of catalytic transformation of ethane-ethylene mixture could provide a better understanding of factors being responsible for very high selectivity of the process.

Experimental and methods

V-Mo-Nb-Te-O_x catalyst, being similar to those used in propane-to-acrylics oxidative conversion, was prepared by a standard hydrothermal method with subsequent thermal treatment in inert gas flow [3, 4, 24].

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The crystallinity and phase composition of the catalyst was determined via X-ray diffraction on a DRON-2 unit (2θ range of 5°to 60°)

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.

The catalysts were tested in ethane oxidation at 300–450°C using oxidant-deficient reaction mixture [75 % C_2H_6 + 25 % O_2] containing no inert diluent [20]. The mixture was fed to the quartz micro-reactor under 1 atm pressure and a space velocity of 900–18,000 h^{-1}. The catalysts were tested in ethane and ethene oxidation at 360–450°C by placing the sample charge (0.1 cm^3; 0.15 g; fraction 0.25–0.75 mm) in a fixed-bed quartz reactor (inner diameter 4.5 mm). A fused quartz (0.1 cm^3; fraction 0.25–0.75 mm) was used as a diluent of the catalyst (1:1). To reduce the time of the gas residence in the hot zone a free space of the reactor tube was filled with a crushed quartz. No catalyst pretreatment in the reactor was done. The fresh catalyst loading was heated up to 360°C in the reaction mixture flow (15 cc/min), and the catalytic testing was repeated 2–3 times at 360°, 420°, 450° and back 360°C, respectively. The outgoing gas flow passed through the glass trap (20°C) for removal of the excess water. Samples of the reactor effluent were injected periodically into a chromatograph equipped with the Porapac-Q column and a catharometer. Catalyst activities were measured with accuracy ±5 % at the ethane conversion from 1 to 30 % for the above-mentioned mixtures of reactants. Ethylene and CO_2 were the main reaction products in all tests, and only traces of acetic acid were detected in the water condensate accumulated in the trap. So, the overall process can be presented by the sum of the two reactions:

$C_2H_6 + 1/2\ O_2 = C_2H_4 + H_2O$;

$C_2H_6 + 7/2\ O_2 = 2\ CO_2 + 3\ H_2O$.

Additional components and impurities were added into the incoming gas flow by introduction of different compounds given below.

Methane influence was studied by adding 15 vol.% CH_4 to the reaction mixture [ethane + oxygen].

Ethylene-containing gas mixtures [13 vol.% O_2 + 87 vol.% C_2H_4] and [20 vol.% O_2 + 18 vol.% C_2H_4 + 62 vol.% C_2H_6] were prepared in the gas cylinders by mixing ethylene of 99.9 %-purity with ethane and technical grade oxygen (98 %).

CO_2 role was studied using gas mixtures [21 vol.% O_2 + 47 vol.% C_2H_6 + 32 vol.% CO_2], [59 vol.% C_2H_6 + 41 vol.% CO_2] prepared in the gas cylinders by mixing ethane of 99.9 %-purity with technical grade oxygen and CO_2.

Methanol influence was studied by introduction of 2000 ppm of CH_3OH into the reaction mixture [ethane + oxygen].

Dimethyldisulfide influence was studied by adding 500 ppm of DMDS to the standard reaction mixture [ethane + oxygen].

Results and discussion

XRD analysis of the catalyst obtained (Figure 1) indicates the presence of well-crystallized M1 phase in accordance with literature data [4]. X-ray diffractogram have more than ten intense diffraction lines, the most intense lines correspond to diffraction angles 2Θ of 7.7°±0.4, 8.9°±0.4, 22.1°+0.4, 26.6°±0.4, 26.9°±0.4, 27.1°±0.4, 28.1°±0.4, 31.2°±0.4, 35.0°±0.4 and 45.06°±0.

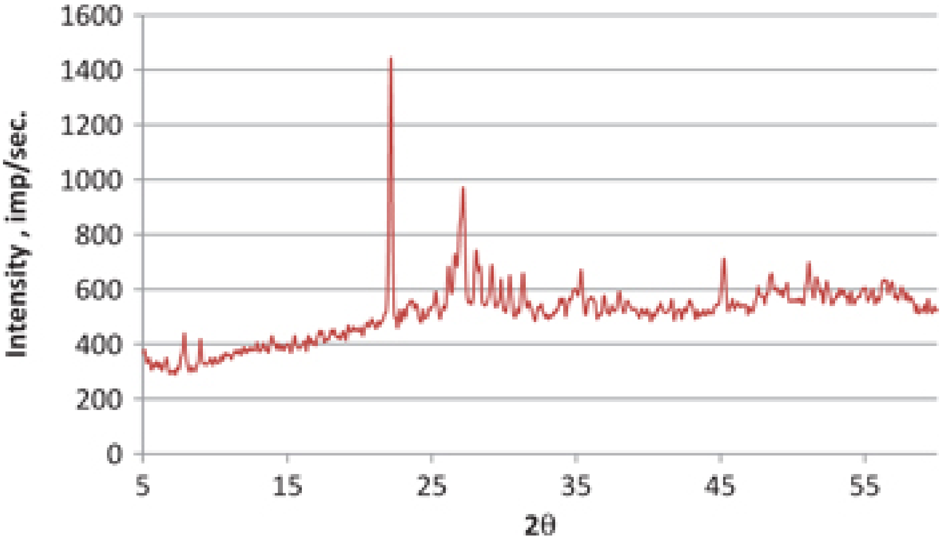

Figure 1: XRD defractogram of V-Mo-Nb-Te catalyst.

Concentrations of elements in catalyst Mo–V–Te–Nb–O according to X-ray microanalysis are (these data were obtained by scanning electron microscope with EDS module): Mo – 55.04 wt%, V – 8.96 wt%, Te – 12.06 wt%, Nb – 10.20 wt%. Thus, the concentrations of elements in quaternary mixed oxide catalyst calculated per 1 atom of molybdenum are: $MoV_{0.29}Te_{0.16}Nb_{0.19}O_x$

Methane admixture

Catalytic testing at temperatures up to 450°C shows that methane is neither involved in the oxidation reaction nor suppress ethane SOD. It acts as a chemically inert mixture diluent. No selectivity loss (98–94 % of ethylene) can be detected in methane presence.

Thus, in oxidative treatment of the (C_2H_6 + CH_4) gas mixture ethane SOD can be realized at temperatures up to 450°C, with methane being a completely inert component of the mixture.

Ethylene admixture

Catalytic oxidation of pure ethylene, by oxygen, was tested under the same conditions used in ethane oxidation. Data received for the same V-Mo-Nb-Te catalyst are compared on Figure 2 and Figure 3. The rate of [ethane-to-ethylene oxidation] exceeds very substantially the rate of the [ethylene-to-CO_2 oxidation]. This fact is clearly illustrated on Figure 4 by plotting the ratio of specific rates of the two reaction steps (k1 – reaction rate of ethane-to-ethylene oxidation, k2 – reaction rate of ethylene-to-CO_2 oxidation) *vs*. temperature. Drop of this ratio with the temperature demonstrates that activation energies of the two steps differ substantially, but even at 450°C the ODH rate exceeds the complete oxidation rate by more than one order of magnitude. As a result, one can expect that the presence of a considerable amount of ethylene in the gas mixture does not suppress noticeably the rate of ethane oxidative dehydrogenation.

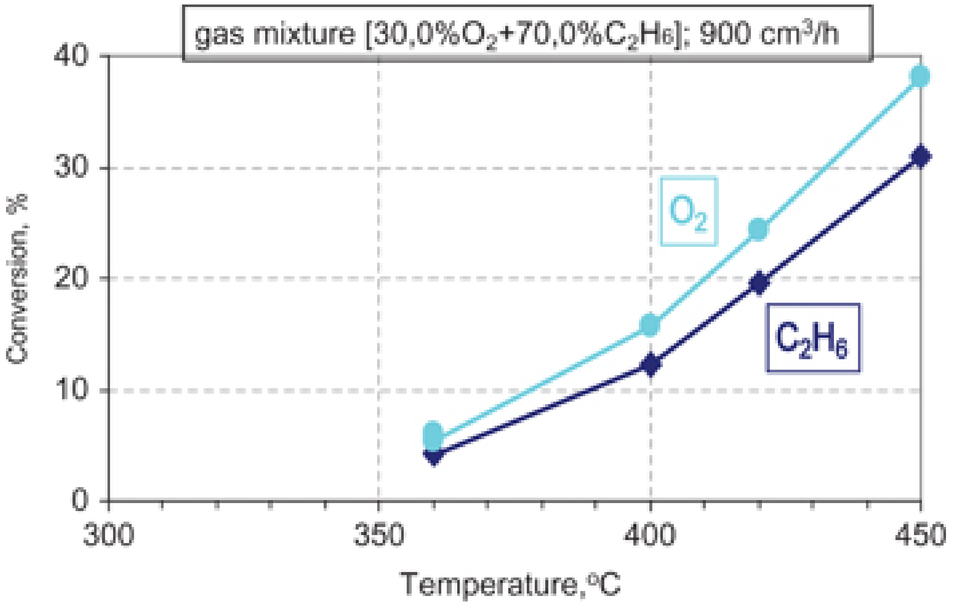

Figure 2: Ethane SOD on the V-Mo-Nb-Te catalyst (145 mg).

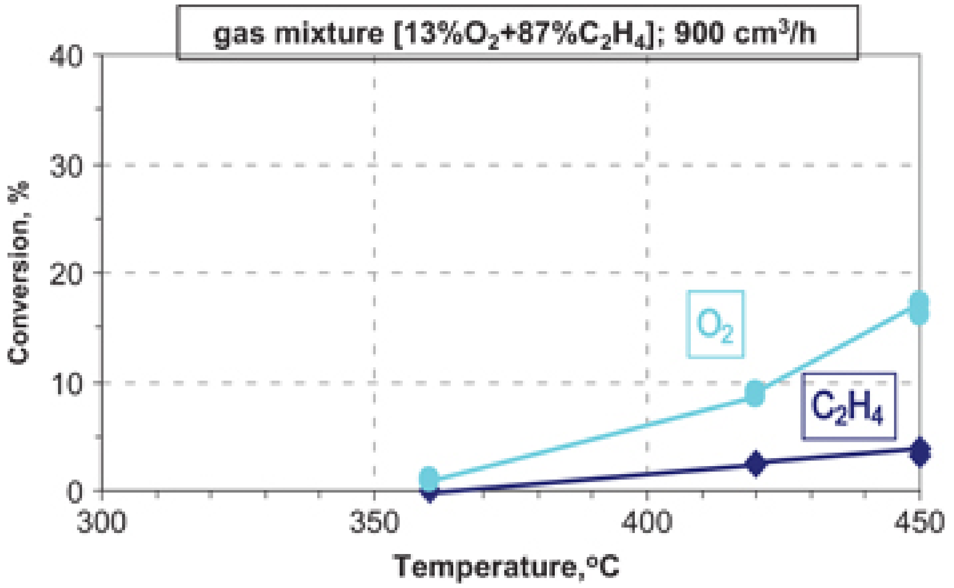

Figure 3: Ethylene oxidation on the V-Mo-Nb-Te catalyst (162 mg).

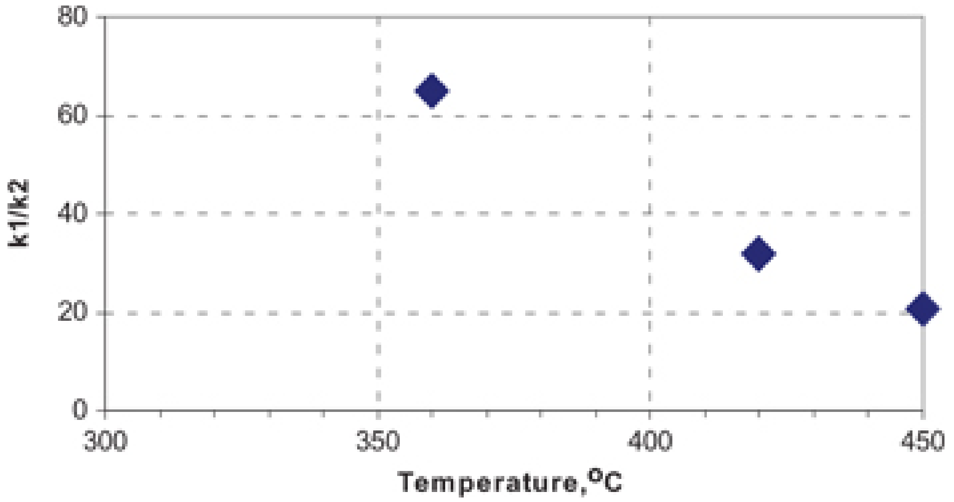

Figure 4: Temperature dependence of the ratio between specific rates of [ethane→ ethylene oxidation] (k_1) and [ethylene→ CO_2 oxidation] (k_2) on the V-Mo-Nb-Te catalyst.

With the triple gas mixture [C_2H_6+C_2H_4+O_2] the comparative testing of ethane and (ethane+ethylene) oxidation on the same catalyst were realized under the identical conditions. As one can see, the presence of a considerable amount of ethylene in the gas mixture does not have a noticeable impact on the rate of ethane oxidative dehydrogenation (Figure 5). In regard to the reaction selectivity (Figure 6), a small decrease in reaction selectivity is observed that could be caused by an additional contribution of the ethylene-to-CO_2 reaction.

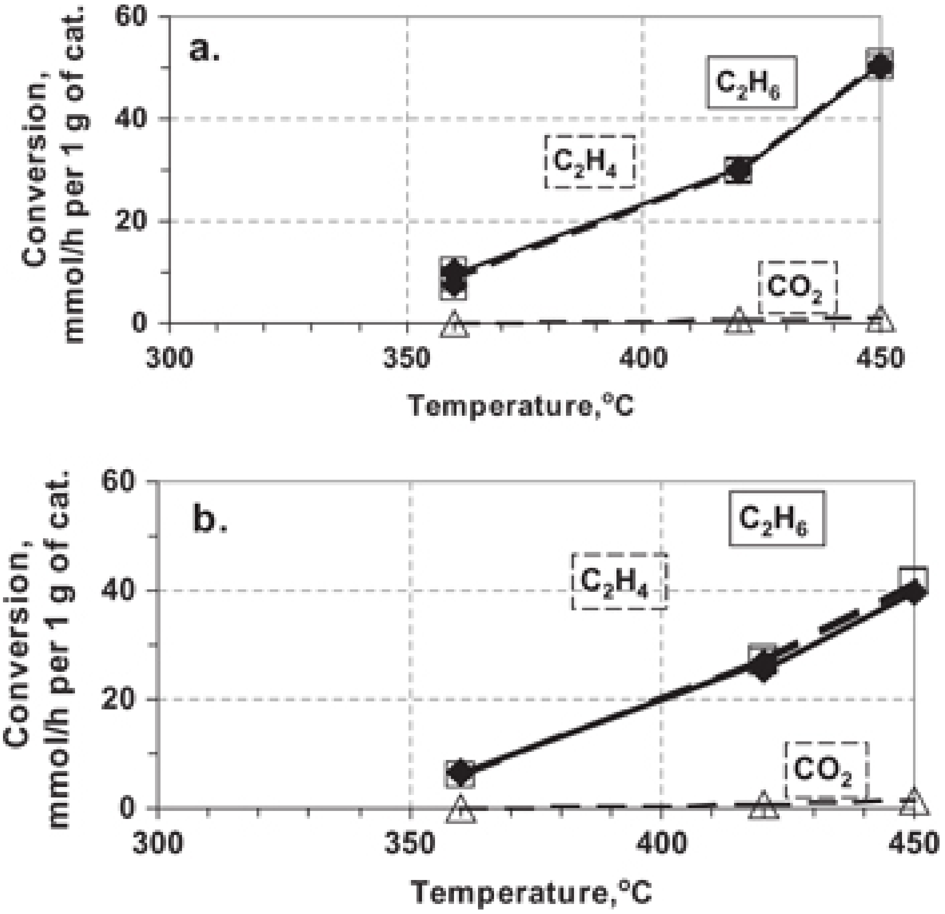

Figure 5: Ethane SOD on the V-Mo-Nb-Te catalyst: (a) – [76,4%C_2H_6+23,6%O_2]; (b) – [61,9%C_2H_6+17,6%C_2H_4+20,5 %O_2]. – C_2H_6; □ – C_2H_4; Δ – CO_2.

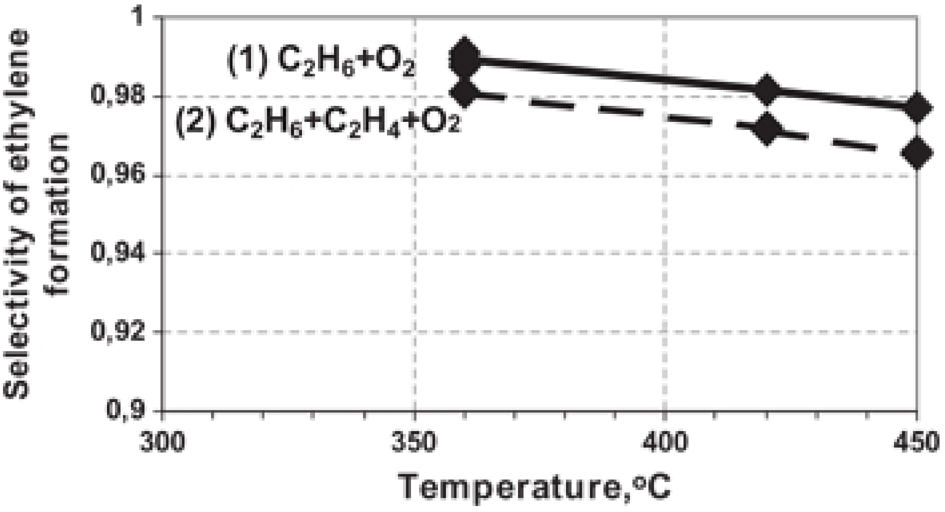

Figure 6: Selectivity of ethylene formation on the V-Mo-Nb-Te catalyst: role of the additional C_2H_4.

It is interesting to note a quite unusual behavior of the quaternary V-Mo-Nb-Te catalyst in oxidation process. The majority of oxidation catalysts provide a faster alkenes oxidation as compared with respective alkanes. On the contrary, the catalyst under study demonstrates an opposite ratio of partial and complete oxidation rates. By other words, the surface of the catalytically active phase contains manly specific sites of partial oxidation with negligible admixture of complete oxidation sites. We suppose that this peculiarity of the catalyst can be related with presence of specific form of oxygen in the structure of the orthorhombic M1 active phase [21–23].

CO_2 admixture

Comparative tests of the catalyst Mo-V-Te-Nb with the binary gas mixture and the mixture containing a large amount of CO_2 (32 %) demonstrate that the influence of this component is detectable but not pronounced. Figure 7 illustrates the influence of CO_2 on the *specific rate* of C_2H_6 to C_2H_4 conversion. Conversion of ethane in the presence of CO_2 decreases by 2–8 % over the studied temperature range 360–430°C (Figure 7). Some small selectivity drop can also be detected (Figure 8). This drop may be explained by a) - the reduced partial pressure of ethane, and/or b) - CO_2 adsorption on active sites. In conclusion, CO_2 plays a minor role hindering slightly catalytic ethane SOD.

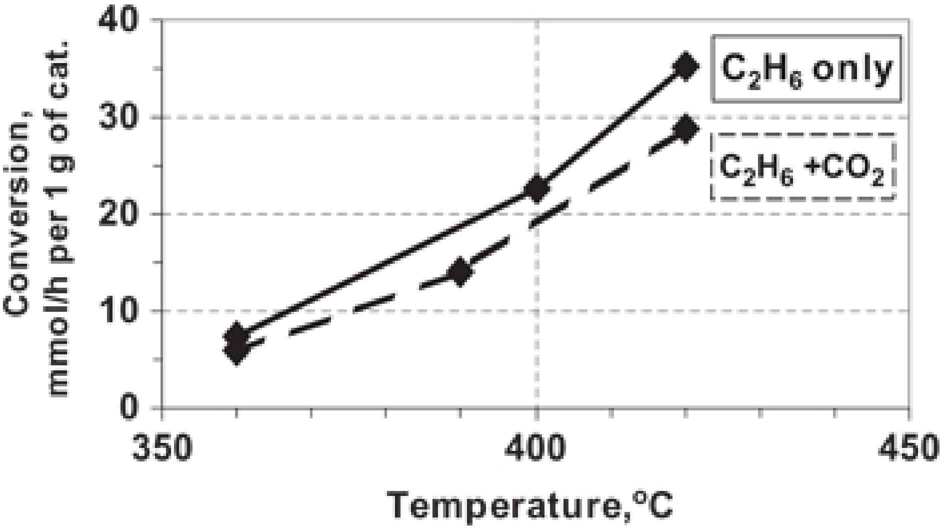

Figure 7: Specific rate of ethane SOD in presence and absence of CO_2 on the V-Mo-Nb-Te catalyst.

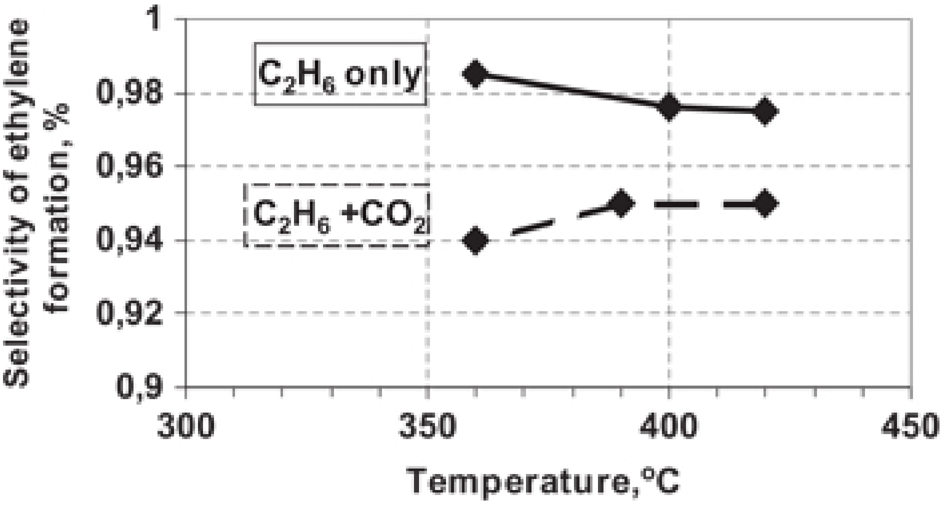

Figure 8: Selectivity of ethylene formation in presence and absence of CO_2 on the same V-Mo-Nb-Te catalyst.

In a low-temperature testing (up to 420°C) no CO_2 consumption from the gas mixture was detected, i. e., carbon dioxide behaved as an inert gas. Testing of the same catalyst was done using the gas mixture [C_2H_6+CO_2] to double-check a possible role of CO_2 as oxidant. No ethylene formation was detected up to 450°C.

Methanol impurity

Comparative testing of ethane oxidation in the presence and absence of methanol (0,2 %) on the same catalyst is realized under the identical conditions and results are given on Figure 9 and Figure 10. As one can see, the presence of methanol admixture (0.2 %) in the gas mixture does not change the rate of ethane oxidative dehydrogenation (Figure 9), (b). As to the change in ethane oxidation selectivity (Figure 10), a negligible drop of selectivity can be explained by small additional methanol-to-CO_2 oxidation. Thus, contamination of the gas flow by small amount of methanol does not reduce both activity and selectivity of the catalyst in ethane SOD.

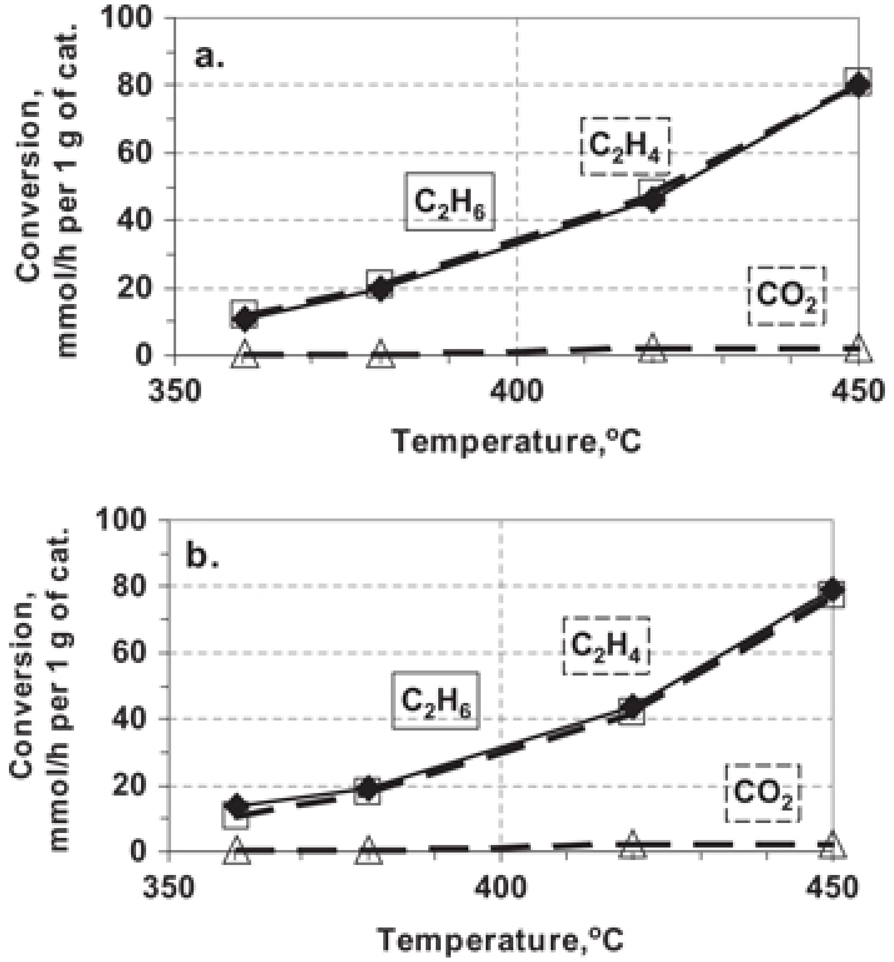

Figure 9: Ethane SOD on the V-Mo-Nb-Te catalyst: (a) – [76,4%C_2H_6+23,6%O_2]; (b) – [72.7%C_2H_6+27.3%O_2+2000 ppm CH_3OH]. – C_2H_6; □ – C_2H_4; Δ – CO_2.

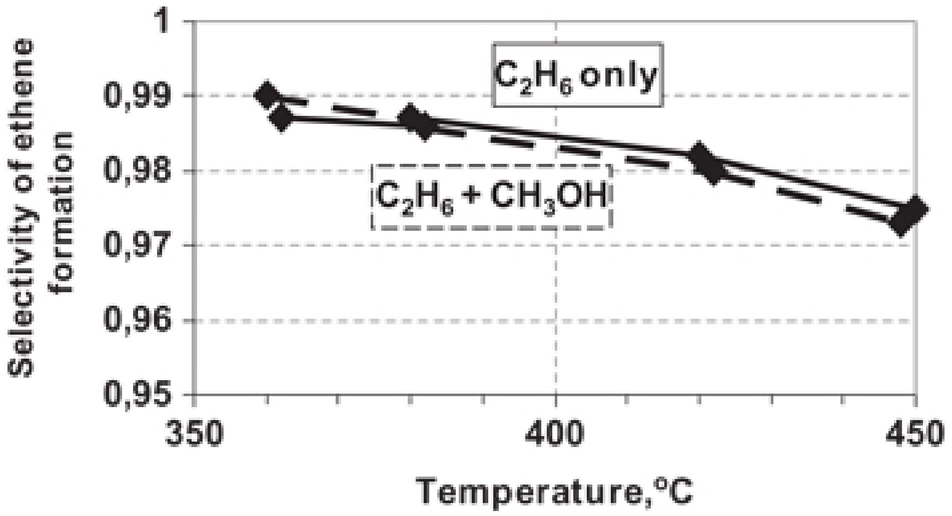

Figure 10: Selectivity of ethylene formation on the V-Mo-Nb-Te catalyst in presence and absence of methanol (2000 ppm).

Sulfur-containing impurity

Results of the catalytic testing in either absence or presence of DMDS for the same catalyst are compared on Figure 11 and Figure 12. No activity/selectivity loss can be detected in DMDS presence (Figure 11 and Figure 12).

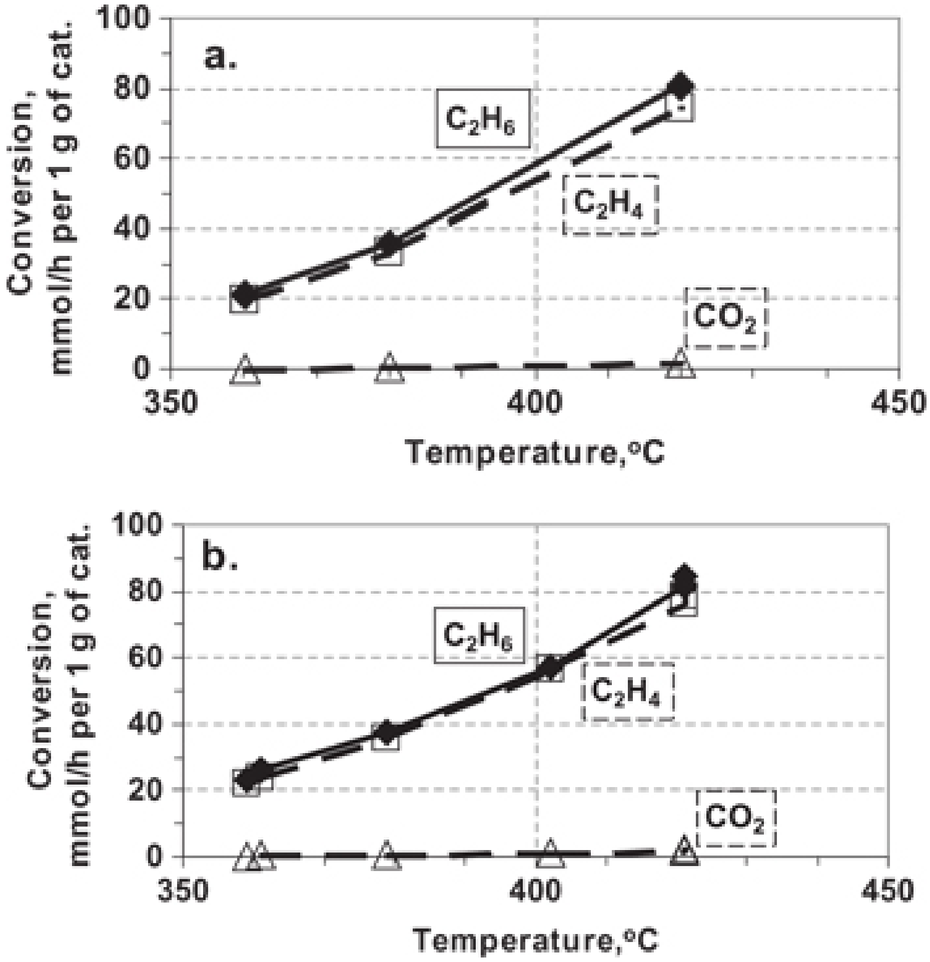

Figure 11: Ethane conversion on the V-Mo-Nb-Te catalyst: (a) – without DMDS; (b) – in presence of 500 ppm of DMDS in the gas flow. – C_2H_6; □ – C_2H_4; Δ – CO_2.

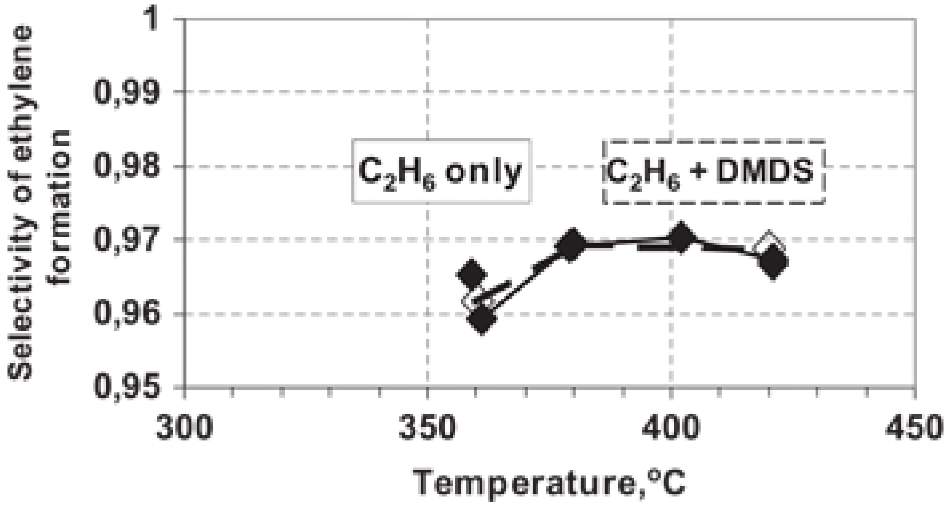

Figure 12: Selectivity of ethylene formation on the V-Mo-Nb-Te catalyst in presence and absence of DMDS (500 ppm) in the gas flow.

Thus, small admixture of S-containing compound does not provoke measurable poisoning effect on selective oxidative dehydrogenation of ethane. However, this result is obtained in a relatively short-term testing (4 h).

Long-term effect (caused, for example, by gradual slow accumulation of sulfates on catalytic surface) cannot be excluded. Another common sulfur containing impurity in ethane is H_2S, but this more reactive compound is not investigated in our work.

Conclusions

Methane serves as a chemically inert diluent of the gas mixture $[C_2H_6 + O_2]$ upon ethane SOD on V-Mo-Nb-Te-O_x. Presence of ethylene in feed stream does not reduce substantially the rate of ethane dehydrogenation but causes some drop of selectivity. CO_2 added is not involved in chemical transformations but suppress slightly ethane conversion and selectivity. Contamination of the gas flow by small amounts of either methanol or DMDS does not reduce both activity and selectivity of the catalyst in ethane oxidative dehydrogenation.

The preliminary results obtained from this work open the way for the use of recycling operation mode as applied to ethane-containing industrial gases for highly selective ethane oxidative dehydrogenation. However, further work on the impact of other industrial impurities, such as H_2S, as well as the impact of impurities on catalyst life-time should be carried out before moving the SOD technology to the next phase of development.

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