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Additional Information

Chemical, Structural and Morphological Changes of MoVTaNb Catalyst during Oxidative Dehydrogenation of Ethane

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ABSTRACT

MoVTeNb mixed oxide is a highly active and selective catalyst for oxidative dehydrogenation of ethane to produce ethylene, which exhibits the so-called *M1* and *M2* crystalline phases. Thermal stability of MoVTeNb catalytic system was assessed under reactions conditions, for this end the catalyst was exposed to several reaction temperatures spanned from 440 to 550°C and the pristine and spent materials were thoroughly analyzed by several characterization techniques. The catalyst's stability limit to operate at reactions temperatures <500°C, since, when reaction temperature is $\geq 500^\circ\text{C}$ brings about the removal of tellurium from the intercalated framework channels of *M1* crystalline phase. Rietveld refinement of XRD patterns and microscopies results point out that the tellurium loss cause the progressive partial destruction of *M1* phase, thus decreasing the active sites amount and forming a MoO_2 crystalline phase, which is inactive in the employed reactions conditions. Raman spectroscopy confirms the MoO_2 phase development in function of reaction temperature. From HRTEM and EDS analyses it was noticed that tellurium depart occurs preferentially from the end sides of the needle-like *M1* crystals, across the [001] plane. A detailed analysis of the solid deposited at the reactor outlet displays that it consists mainly in metallic tellurium; hence, the tellurium detaching is carried out by means of a reduction process of Te^{4+} to Te^0 due to a combination of reaction temperature and feed composition. In order to keep the catalytic performance exhibited by MoVTeNb mixed oxide, hot spots along the reactor bed should be avoided or controlled for maintaining the catalytic bed temperature <500°C.

KEYWORDS: *Oxidative dehydrogenation; Ethane; Ethylene; Thermal stability, M1 and M2, MoO₂.*

1. INTRODUCTION

Ethylene is the keystone of the petrochemical industry being also the main building block as well as the major feedstock for polymers production. Currently, most of ethylene commercialized in the world is obtained by pyrolysis (steam-cracking) of different hydrocarbon streams; also fluid catalytic cracking (FCC) process and catalytic dehydrogenation of ethane contributes marginally. Ethylene market is expected to increase in the coming years, since ethylene's demand is related to population growing.¹ Steam-cracking is carried out at high temperatures ranging from 800 to 900 °C and, hence, the energy consumption of the process is considerable.² Apart from consuming a large amount of energy and requiring a special metallurgy for the furnace internal components, a high temperature steam-cracking operation increases the occurrence of side reactions decreasing the global selectivity to ethylene and resulting in the formation of a large diversity of byproducts such as acetylene, hydrogen and methane, etc., which are difficult to be separated from the main reactor effluent, requiring of complex downstream separation processes.^{3,4}

On the other hand, an unfavored thermodynamic equilibrium restricts the catalytic dehydrogenation of ethylene yield at moderate temperature (<600°C).⁵ Even though catalysts used to increase ethane conversion and ethylene selectivity, they are very susceptible to deactivation by coke.⁶ Restoring the catalyst's activity is possible, but requires a special engineering configuration, which appreciably augments the operation costs.

Related to ethylene, there is a strong interest in investigate alternative ways of production that overcome the disadvantages characterizing steam-cracking and catalytic dehydrogenation processes.

For several years, oxidative dehydrogenation of ethane (ODH-C₂) has been studied as a plausible technologic alternative for ethylene production. ODH-C₂ is performed via a

heterogeneous catalyzed process in which ethane reacts with an oxidant species.^{4,5,7} Several advantages are detected when contrasting ODH-C₂ with direct dehydrogenation: (i) no thermodynamic limitations exist, (ii) reactions are exothermic thus avoiding the need to supply heat by external means, (iii) the number of products is limited and easy to be tracked and handled, and (iv) no coke formation occurs.⁸

Producing ethylene via ODH-C₂ at commercial scale is still a challenge. It is evident that a basic key requirement for this reaction is having a catalyst with adequate properties to produce selectively ethylene and minimize CO_x formation. It is in fact reported that in an economical attractive industrial scenario for ODH-C₂, ethylene selectivity should be higher than 90 % with ethane conversion ranging from 60-80 %, at temperatures lower than 500 °C.^{2,3,9}

High selectivity to ethylene is one of the most important features of a suitable catalyst, not only for economic feasibility, but also because the combustion reactions responsible for the formation of CO and CO₂ are *ca.* 8 and 13 times more exothermic, respectively, than ethylene production from ethane.⁹ This would represent an important issue for operational reactor control, due to the hot points generated by the aforementioned combustion reactions.

In this context, a large variety of catalytic systems have been reported in the literature. So far, one of the most outstanding catalysts for the ODH-C₂ to ethylene is a multicomponent catalyst based on MoTeVNb mixed oxides, which has been described and studied by several research groups.⁹⁻¹⁶ Certainly, the catalyst must exhibit a multifunctional assortment of properties, since their catalytic performance depends on them. Thus, the crystalline phases play a crucial role to create and control the catalytic centers required.

These MoTeVNb materials consist of mixed oxides mainly composed of the *M1* and *M2* crystalline phases, as well as minor amounts of phases, like Mo₅O₁₄-type structures or binary MoV and MoTe oxides. *M2* shows hexagonal phase with space group *P6mm*, this phase has been

determined as practically inactive in the ODH-C₂ reaction. The orthorhombic *MI* phase, space group *Pba2* (No. 32) is built from center-occupied pentagonal rings that are linked together by corner-sharing MO₆ octahedrons, (M= Mo, V), which are assembled in the [001] plane forming characteristic hexagonal and heptagonal rings hosting Te-O units. Niobium is preferentially located in pentagonal bipyramidal environment. However, due to a certain chemical flexibility of the phase, octahedral positions may also be occupied by Nb in *MI* with higher Nb content. A bronze-like channel structure is established by stacking layers of the polyhedrons in the [001] direction resulting in a needle-like crystal morphology in which the [001] planes are arranged perpendicular to the length axis of the needle. It has been suggested that terminating [001] planes of the *MI* phase contain the most active and selective surface sites for ODH-C₂.¹⁰⁻²⁴

This assumption has encouraged worldwide research on the crystalline structures and physicochemical properties of the *MI* phase by means of several characterization techniques.^{13,}
²³⁻³³ In this sense, López-Nieto et al. have reported an important tellurium loss during thermal treatment activation of catalyst, which is commonly performed at 600 °C under nitrogen.³⁴ Indeed, the Mo/Te ratio increases when increasing the niobium oxalate content, since, oxalate anions act as reducing agent, which enhances the reduction degree of tellurium cations, rendering it instable and easily removal from the crystalline structures. Because of the metallic tellurium has a low temperature melting point (ca. 450 °C).

Notwithstanding, the issues showed by the presence of tellurium; it seems to be indispensable in most of the high efficient catalytic systems reported to date for the ODH-C₂ to ethylene. Consequently, the relatively high susceptibility of tellurium to reducing atmospheres, together with the large amount of metal that is lost during the thermal activation stages, appears to be a restriction for a catalyst scaling-up to industrial level. This problem would be always latent in industrial practice since, during operation, the reaction mixture can be composed of

ethane diluted in nitrogen, i.e., a reductive mixture which, in the presence of hot-spots would favor the reduction and further loss of tellurium with the consequent gradual decay in the catalytic properties of the solid. However, few reports are available about the thermal stability of MoVTeNb catalyst when it is exposed to severe operation conditions.

Therefore, this work is focused to study the chemical, structural and morphological changes occurring over a MoVTeNb catalyst, when it is exposed to several reaction temperatures (440, 480, 500 and 550°C) and their impact on the corresponding catalytic properties, in order to set parameters for keeping the catalytic performance exhibited by these materials in the ODH-C₂. For this end, catalytic tests were carried out in a lab-scale reactor and then spent materials were examined by using different characterization techniques.

2. EXPERIMENTAL

2.1 Catalysts preparation

MoVTeNb mixed oxide with Mo:V:Te:Nb=1:0.24:0.24:0.18 nominal atomic ratios, was prepared by the slurry method, which comprises the following steps: 1) an aqueous solution containing tetra-hydrated ammonium heptamolybdate (MERK, 99%), telluric acid (Aldrich, 98 %) and ammonium metavanadate (Sigma-Aldrich, 99.5%) was mixed under continuous stirring, at 80 °C; 2) In parallel, an aqueous solution containing niobium oxalate (ABCR laboratories, 99%) and oxalic acid (Aldrich, 98%) was also prepared, at 80 °C. The solution 2) is slowly added to solution 1) under a vigorous continuous stirring. The resulting slurry was cooled down to room temperature and then, the pH was adjusted to 2.5 by using 1M nitric acid solution. The acidified slurry was subsequently dried in a rotavapor device, at 50 °C and 27 kPa. The resulting solid was dried overnight at 100 °C and finally thermally treated at 600 °C for 2 h under nitrogen. The material obtained was labeled as MoVTeNb-F, where F stands for pristine material.

The pristine catalyst (MoVTeNb-F) was subjected to a series of catalytic tests spanning temperature from 440 to 550 °C. Samples resulting from such tests, denoted as spent catalysts, were recovered for characterization. Spent catalysts were coded as MoVTeNb-S440, MoVTeNb-S500 and MoVTeNb-S550, the number representing the reaction temperature in Celsius degrees used in the test.

2.2 Catalytic testing procedure

The catalytic experiments were performed in a semi-automatized lab-scale set-up, equipped with a 10 mm internal diameter/40 mm length fixed-bed quartz tubular reactor, operated isothermally, atmospheric pressure and integral regime. All tests were performed feeding the reactor with a mixture of ethane (C₂) and oxygen (O₂), as well as nitrogen (N₂) as diluent. The N₂ was also employed as internal standard. The purity of ethane, oxygen and nitrogen utilized in the experiments were 99.7 vol%, 99.996 vol% and 99.999 vol%, respectively. The reactor effluent was analyzed periodically on-line by gas chromatography (GC) detailed set up is reported in reference 9.

The amount of catalyst was 0.6 g (150 microns average size) and the fed to the reactor was C₂/O₂/N₂ with a molar ratio of 9/7/84. Reaction temperatures ranged from 440 to 550 °C and the space-time (W/F_{ethane}^0) was maintained at 35 g_{cat} h(mol)⁻¹. A blank experiment carried out at 550 °C confirmed the absence of ethane conversion.

Ethane conversion and ethylene selectivity were defined on a carbon basis. Ethane conversion was calculated by equation 1

$$X_{\text{C,ethane}} = \frac{G_{\text{C,ethane}}^0 - G_{\text{C,ethane}}}{G_{\text{C,ethane}}^0} \times 100 \quad (1)$$

where, $G_{C,ethane}^0$ and $G_{C,ethane}$ indicate the mass flow of ethane at the inlet and outlet of the reactor, respectively.

Selectivity to ethylene and oxidation products, CO and CO₂, were calculated considering the carbon mass in component i formed per mass of carbon in ethane converted according to equation 2.

$$S_{C,i} = \frac{G_{C,i}}{G_{C,ethane}^0 - G_{C,ethane}} \times 100 \quad (2)$$

The ethane flow was measured at standard conditions, *i.e.*, 1 atm (101.32 kPa) and 20 °C. The flow at the reactor outlet was quantified via the internal standard method according to equation 3.

$$F_i = \frac{F_{N_2}^0 M_{N_2}}{A_{N_2} C_{f_{N_2}}} \times \frac{A_i C_{f_i}}{M_i} \quad (3)$$

where, F_i is the outlet molar flow rate of compound i , calculated from molecular mass (M), GC-integrated area (A) and GC-calibration factor (C_f) of product i ; the corresponding values of nitrogen were used as internal standard ($F_{N_2}^0$ is the molar flow rate).

The catalytic performance of MoVTenb-S550, coming from the highest temperature test, was measured again in order to investigate changes in catalytic properties related to the corresponding pristine sample.

2.3 Characterization techniques

2.3.1 X-ray diffraction

The X-ray power diffraction patterns of pristine and spent catalysts were recorded in a Siemens D-500 diffractometer, provided with a θ - θ configuration and a graphite secondary beam monochrome. Diffraction intensity was measured from 4 to 60° using a 2θ step of 0.02° for 8 s per point, using $\text{CuK}\alpha_{1,2}$ radiation with a wavelength of 1.5418 Å as well as a power of 40 kV and 40 Ma. The unit cell parameters of *M1*, *M2* and MoO_2 were refined by full pattern fitting according to the Rietveld method by using the *M1* and *M2* crystallographic information reported by DeSanto et al.^{18,19} employing the MAUD Bruker program.

2.3.2 Electron Microscopies, HRTEM and SEM.

Samples were subjected to a high resolution transmission electron microscopy (HRTEM). Micrographs were obtained in a TITAN 80-300 with Schottky type field emission gun operating at 300 kV. The resolution point and information limit were better than 0.085 nm. HRTEM digital images were obtained using a CCD camera and Digital Micrograph Software from GATAN. Additionally, elementary composition was determined by energy dispersive X-ray spectroscopy (EDS) with an EDAX spectrometer fitted to the TEM. In order to prepare the materials for analysis, samples in the powder form were ultrasonically dispersed in ethanol and then supported on holey carbon coated copper grids.

The surface morphology and elemental composition were obtained by scanning electron microscopy (SEM). Images of samples were taken in a Nova-200 Dual-Beam Microscope equipped with a Schottky type field emission gun using a resolution of 1.1 nm. An X-ray Si (Li)

ultrathin window energy dispersive spectrometer (EDS) from EDAX was coupled aimed at detecting elements from the beryllium onwards.

2.3.3 Raman Spectroscopy

The raman spectra were recorded using an Yvon Jobin Horiba (T64000) spectrometer, equipped with a confocal microscope (Olympus, BX41) with an Ar ion laser operating at 514.5 nm at a power level of 10 mW. The spectrometer is equipped with a CCD camera detector.

The samples were excited by the 514.5 nm line of Ar⁺ laser (Spectra Physics model 171) with a laser power of 2.5 mW. The following spectrometer characteristics were used: microscope objective 50^x, spectral resolution 2.5 cm⁻¹; integration time 20s per spectrum; and 50 scans. Raman spectra were obtained at different points in each sample to determine homogeneity and/or heterogeneity of the sample. The spatial resolution of each analysis was about 0.4µm.

3. RESULTS AND DISCUSSION

3.1 Catalytic testing

3.1.1 Conversion and selectivity versus time behaviour over pristine catalyst

At the reaction conditions used, ethylene, CO and CO₂ were the only reaction products detected in the reactor effluent during the ODH-C₂. The contribution of these products to the reactor effluent composition, in fact, evolved in the following order: ethylene >> CO > CO₂. However, the relative amount of these compounds depends upon the specific reaction conditions, e.g., reaction temperature, space-time, etc.

Figure 1 shows ethane conversion and ethylene selectivity as a function of time on stream. From this plot, at the studied operating conditions, i.e., 440 °C and C₂/O₂/N₂=9/7/84 inlet molar ratio, the MoVTenb mixed oxide catalyst exhibited a remarkable stability. No significant

changes in conversion or selectivity were detected during the repetition of three run tests; with 7 hours of time on stream each one, using the same catalytic material. Notice that the catalyst exhibited a conversion of ethane of around 45 % for a $W/F_{\text{ethane}}^0=35 \text{ g}_{\text{cat}} \text{ h/mol}_{\text{ethane}}$, which reached a value as high as 65 % for $W/F_{\text{ethane}}^0=70 \text{ g}_{\text{cat}} \text{ h/mol}_{\text{ethane}}$. Aside, selectivity to ethylene is remarkably high reaching a value of ca. 90-93 %. The good stability in the catalytic performance of the sample indicates that its active sites remain unchanged during the reaction tests.

3.1.2 Pristine catalyst versus spent catalyst performance

The exothermic character of main and side reactions during the ODH-C₂ may lead to the formation of hot spots along the reactor bed, which at the end, may damage the catalyst crystalline structure altering the corresponding catalytic behavior. With the end of assessing the thermal stability of the MoVTeNb mixed oxide, the catalytic performance of pristine sample (MoVTeNb-F) was measured at space-time of $35 \text{ g}_{\text{cat}}\text{h/mol}_{\text{ethane}}$ and varying the temperature within the range 440 to 550 °C. In order to evaluate the possible damage of physicochemical properties in spent samples, after catalytic test at 440, 500 and 550 °C, the samples were recovered and characterized. On the other hand, a MoVTeNb mixed oxide sample was evaluated at increasing reaction temperatures, taking 3 analyses at each temperature. When the ODH-C₂ reaction was over, the reactor was cooled down and its catalytic performance, corresponding now to a spent catalyst (MoVTeNb-S), was measured again at the same 440-550 °C temperature range. The deviations on the catalytic performance of the MoVTeNbO-F and MoVTeNbO-S500 samples are then discussed on the basis of steady-state experimental data.

Figure 2 displays plots of ethane conversion as well as selectivity to ethylene, CO and CO₂ as a function of reaction temperature for pristine and spent MoVTeNb mixed oxide catalyst. It is observed in Figure 2a that, from 440 to 520 °C, both catalysts exhibit a linear increase in the

ethane conversion. In the case of the pristine sample, an augment in reaction temperature from 520 to 550 °C did not lead to an increase in ethane conversion, even a slight decrease in the ethane conversion, from 61 to 59 mol%, was observed. A small decreasing in ethylene selectivity, with the concomitant augment in CO_x selectivity was detected. This unexpected behavior might be related to a catalyst damage caused by the high reaction temperature (520 °C) used in the preceding reaction stage.

Concerning products distribution, Figures 2b-d show that, over both pristine and spent catalysts exhibit a monotonically increase in the selectivity to combustion products, (CO and CO₂) with temperature, in detriment of that to ethylene. At the end of the test when removing the catalyst from the reactor, a silver color solid deposit was visually detected on its outlet connecting tube, particularly when reaction is conducted above 480 °C. Due to a temperature profile in the furnace that heats the reactor, the temperature at the reactor outlet is significantly lower than the one at the catalyst bed zone, which let to observe this deposit.

In relation to the pristine catalyst, the spent catalyst is appreciably less active for ethane conversion, in particular, when reaction is performed far below 520 °C. In relative terms, the spent catalyst is ca. 41 % less active for ethane conversion than the pristine one, when comparing the catalytic results at 440°C. Concerning the selectivity reaction products, differences are, however, fairly less evident than those found for ethane conversion and, actually, detectable only at temperatures below 480 °C. In fact, at 440 °C the temperature at which a maximum ethane conversion deviation is detected, the spent catalyst is around 4percentage points less selective to ethylene, compared with the pristine catalyst; while CO₂ selectivity is slightly reduced as observed in Figure 2d. From these results, it is inferred that the loss of ethane conversion in the spent catalyst should be essentially associated to a decrease in the active sites density and not necessarily to the transformation of active and ethylene sites into non-selective new ones.

3.2 *Pristine and spent catalyst analyses*

In order to investigate on changes in the MoVTenb catalyst after reaction, up to a temperature as high as 550 °C, physicochemical properties of pristine catalyst were compared with corresponding ones of a series of spent catalysts.

3.2.1 *X-ray diffraction*

XRD diffraction patterns of MoVTenb mixed oxide in the pristine and spent form, the latter subjected to a catalytic test at 440, 500 and 550 C, are comparatively shown in Figure 3A. The experimental and simulated XRD spectra, by using Rietveld method, are included in this Figure. The calculated distribution of phases (wt %), as well as the *M1/M2* weight ratio, is shown in Table 1. Diffraction lines located at $2\Theta = 6.6, 7.7, 8.9, 22.1$ and 27.1° corresponding to orthorhombic $\text{Te}_2\text{M}_{20}\text{O}_{57}$ ($\text{M} = \text{Mo}, \text{V}, \text{Nb}$) *M1* phase and those at $2\Theta = 22.1$ and 28.1° associated to orthorhombic distorted HTB-type $\text{Te}_{0.33}\text{MO}_{3.33}$ ($\text{M} = \text{Mo}, \text{V}, \text{Nb}$) *M2* phase were detected in the MoVNbTe-F, vide Figure 3a.^{18,19,26,35} The MoVNbTe mixed oxide, commonly referred to as the *M1/M2* system, is a composite, in which the referred *M1* crystalline structure has been proposed to be critical for an optimal selectivity during ODH- C_2 conversion.²⁹⁻³³ As reported in Table 1, *M1* is the major crystalline phase present in this catalyst; 95 wt% versus only 5 wt% of *M2* crystalline phase. *M1* has an orthorhombic polyhedral network-type molybdenum bronze structure with a framework similar to that of Mo_5O_{14} and $\text{Mo}_{17}\text{O}_{47}$.¹⁹ This phase can be also described with the generic formula $(\text{TeO})_{1-x}(\text{Mo},\text{V},\text{Nb})_{10}\text{O}_{28}$, wherein the TeO component is intercalated into framework channels. By analogy with the generic description of the *M1* formula, the formula for *M2* can be written as $(\text{TeO})_{2-x}(\text{Mo},\text{V},\text{Nb})_6\text{O}_{18}$.

On the other hand, Figure 3b shows the XRD pattern of sample MoVTenb-S440, a spent mixed oxide subjected to reaction at 440 °C. This sample shows a XRD pattern very similar to

that exhibited by the corresponding pristine sample. Moreover, Rietveld refinement showed the same *M1* and *M2* crystalline phases composition. Therefore, at the particular reaction conditions studied, the MoVNbTe-S440 spent mixed oxide did not exhibit an appreciable change in its crystalline structure, which is in agreement with the catalytic behavior reported in Figure 1. However, when comparing the XRD pattern of pristine catalyst with that of catalysts after catalytic testing at 500 °C (sample MoVTeNb-S500, Figure 3c) and 550 °C (sample MoVTeNb-S550, Figure 3d), differences are evident. From XRD spectra can be observed that increasing reaction temperature to values of 500 °C or higher leads to changes in the crystalline structure of the pristine solid. From XRD point of view, after catalytic test at 500 °C (vide Figure 3c), the formation of monoclinic MoO₂ phase (ICDD 04-007-2356) is observed apart from the presence of *M1* and *M2* phases. On the basis of the relative intensity of the reflections lines of monoclinic MoO₂ phase in Figures 3c and 3d, it is clear that increasing the reaction temperature up to 550 °C results in a more severe degradation of the structure of the MoVTeNb mixed oxide. After ODH-C₂ reaction at 500 °C, in the MoVTeNb mixed oxide was measured 10 wt. % of MoO₂, which reached 24 wt. % in MoVTeNb-S550. Considering the *M1/M2* weight ratio presents in the MoVTeNb-S550 (*M1/M2*=8) is evident that the formation of MoO₂ crystalline phase mainly comes from of destruction of *M1* crystalline phase.

3.2.2 HRTEM and SEM analysis of pristine and spent catalysts

SEM image of the pristine sample shows the typical morphology of *M1* phase, i.e., agglomeration rod-like, and *M2* phase, i.e., platelet-like, as illustrated in Figure 4a.^{26,29,36} The morphology of the spent catalyst tested at 440°C is rather similar to that of the pristine catalyst (Figure 4b), which is consistent with what observed in the XRD analysis. The spent catalyst produced during the test performed at 500°C, however, shows a different morphology (Figure 4c) compared with the

pristine and spent catalyst tested at 440°C samples. It is particularly observed in sample MoVTeNbO-S500 that the proportion of needle-like *MI* phase agglomeration decreases while sintering of the sample is noted. Apparently, atoms from sample diffuse across the boundaries of the particles fusing the particles together and creating solid agglomerates. Such a phenomenon is even more pronounced in spent sample tested at 550 °C (Figure 4d), corresponding to a behavior also observed through the XRD analysis (Figure 3) wherein a rise of diffraction peaks corresponding to MoO₂ phase is detected.

HRTEM image in Figure 5a corresponding to the pristine catalyst shows well defined rod-like particles together with other ones with an irregular morphology. A larger magnification of the selected zone shows more clearly the rod-like particles and the crystallinity of the solid (Figures 5b and c). In contrast, the sample evaluated at 550°C, exhibits a different morphology with more irregular particles compared with the pristine sample, as can be observed in Figure 5d. In fact, sample MoVTeNbO-S550 is composed of longer and thinner particles which are easily identified in the image of Figure 5e. Additionally, a certain loss of crystallinity along with the segregation/separation of the rod-like particles is noted, as illustrated in Figure 5f.

In order to study the loss of crystallinity in the spent catalyst tested at 550 °C, EDS and HRTEM were done in crystals with rod-like morphology (Figure 6). This kind of morphology indicates the presence of *MI* phase. Table 2 contains information of EDS chemical analyses were carried out at the center and at the ends of a long crystal. The areas of crystal where the elementary analyses were taken are those circled. From data of Table 2, it is worth to note that the chemical composition across the crystal is not homogeneous. The chemical composition measured at the center of the crystal, i.e., MoV_{0.15}Te_{0.09}Nb_{0.19}, is not far from that obtained by atomic absorption spectroscopy, i.e., MoV_{0.25}Te_{0.11}Nb_{0.16}. Whereas, that measured at the ends of the crystal presents a lower content in Te and Nb respect to central part of crystal. Actually, the

chemical composition at the both ends of crystal is essentially the same, $\text{MoV}_{0.16}\text{Te}_{0.035}\text{Nb}_{0.10}$, indicating a loss of around 68 % Te and 37.5wt% Nb compared with values at the center of the crystal. So that, it is likely that, under reducing atmosphere and high temperature (≥ 500 °C) in the catalytic zone, Te reduction occurs preferentially across [001] zone axis of *M1* phase. This seems to be associated to a higher reactivity of this plane as suggested in the literature.^{17,18,20,21} On the other hand, HRTEM were obtained for the same catalyst, at the ends of several crystals with rod-like morphology (*M1* phase). Figure 7a shows crystalline material, with damages associated to Te removal and his corresponding SAED pattern in Figure 7b. Surprisingly, contrary to the typical series of spots, the SAED pattern appears like a series of small concentric lines; actually these elongated spots are composed of a set of spots. This remarkable finding suggests that this kind of SAED pattern is showing the decomposition of *M1* phase, and probably *M2* phase, into MoO_2 phase, as established by the XRD of this sample. The inset profile showed in Figure 7b, confirms that the elongated spot is composed of a set of spots. The innermost spot, with interplanar atomic distance of 4.03 Å, would correspond to both *M1* or *M2* phases, while the last spot at 3.3 Å indicates the presence of atomic planes associated to MoO_2 phase, the latter also observed by XRD. The interpretation of this SAED pattern allows us to state that a fraction mainly of the original *M1* decomposes to others phases by a contraction of the original crystal, but keeping the same habitat and orientation comparable to an epitaxial growth, and together with the original phases cause the elongated spots. Extra phases, as evidenced by XRD study, correspond to MoO_2 , but probably also to MoO_3 , Mo_5O_{14} , $(\text{Mo}_{0.93}\text{V}_{0.07})_5\text{O}_{14}$ or $\text{Mo}_{0.97}\text{V}_{0.95}\text{O}_5$ phases, present in small amounts in the spent sample, and therefore, not clearly detected by XRD technique.

3.2.2.1.1 HRTEM and EDS of detached solid from the catalyst.

The silver color deposit formed at the reactor outlet after the catalytic test at higher temperature was recovered and then analyzed by HRTEM and EDS. Figure 8a displays a typical low magnification image of this material, species with sharp needles morphology are observed. The lattice-fringe of parallel planes, observed in the high magnification image (Figure 8b) was identified as metallic tellurium. The EDS of such particles confirmed that these sharp needles particles are constituted by metallic tellurium. They essentially consist of Te (98 wt %), with the other 2 wt % corresponding to V and O (Figure 8c). The loss of Te might be related to the combination of the existence of a reducing atmosphere and a high temperature ($>500\text{ }^{\circ}\text{C}$) in the reactor zone. The loss of Te during the MoVTeNbO mixed oxide activation step, have been explained by Lopez-Nieto *et. al.* by presence of oxalate ions in the Nb source, which would reduce the tellurium to metallic Te; then it is detached from the solid by melting.³⁴ In the present study, the loss of tellurium during the ODH-C₂ reaction at high temperature ($>500\text{ }^{\circ}\text{C}$), can be also associated to a reduction reaction. The presence of ethane and nitrogen in the mixture feed, in combination to a high temperature, favor the reduction of Te from Te⁴⁺ to Te⁰. Since Te⁰ has a melting point of ca. 450 °C, it is easily removed from the catalyst and deposited on the reactor exit. As observed in XRD study, the tellurium removal from the intercalated framework channels of *M1* phase brings about the partial destruction of MoVTeNbO mixed oxide with a simultaneous formation of MoO₂ phase. The loss of long-range order in the low angle peaks ($5 \leq 2\theta \leq 10$), related to the superstructure of *M1* phase, evidence also the detachment of Te from *M1* superstructure. Although, some detachment of Te from *M2* phase, however, cannot be discarded.

It must be noticed that MoVTeNbO-F sample is a mixed oxide chemically and structurally stabilized via a thermal treatment procedure. This material was actually heat-treated under nitrogen flow at 600 °C for 2 h. As explained here above, during such a thermal treatment an important loss of tellurium from this activated sample, as metallic tellurium, has been reported.³⁴

Although this second loss of Te, from the highly active and selective MoVTeNb mixed oxide catalyst, during the ODH-C₂ reaction has been only observed at high temperature (≥ 500 °C), it is an important point to consider in the scale-up of ODH-C₂ process. The high exothermicity of this reaction, and mainly those of secondary CO_x reactions, can facilitate the formation of hot-points, which could irreversibly damage the catalyst. The removal of Te from catalyst not only decreases the Te/(Mo+V+Nb) ratio but also modifies the crystal phase composition. Accordingly, the nature of the crystalline phases and the catalytic performance of heat-treated materials strongly depend on the final chemical composition of catalysts.

As a general trend, the ethane conversion decreases, without a significant loss of ethylene selectivity, when enhanced the loss of tellurium and the concomitant MoO₂ formation. It means that first; Te has an important role in both the *MI* crystalline phase stabilization and the formation of active sites also, and second the MoO₂ crystalline phase will be a spectator in the ODH-C₂ reaction.

At this point, although Ueda et al.³⁷ have shown that it is possible to obtain the *MI* phase by hydrothermal synthesis without tellurium (Mo–V based catalyst), it has been established that Te⁴⁺ plays an important role in the stabilization of the hexagonal channels of this phase.^{29, 38-43} Then, the role of Te in the most active and selective catalysts should not be directly associated to the ethane activation but to the formation of an active and selective crystalline phase, i.e. Te₂M₂₀O₅₇,⁴⁴ for the oxidative activation of both ethane and propane and, additionally, for the elimination of non-selective Mo-containing crystalline phases, especially MoO₂ and/or other MoVNbO related compounds, generally proposed in Te-free MoVNbO mixed oxide catalysts.^{25,}

3.2.3 Raman spectroscopy

The Raman spectra of pristine and spent catalysts are shown in Figure 9. Since the XRD spectrum of MoVTenbO-S400 spent catalyst was very similar to that of pristine sample, only the spectra of spent samples catalytically tested at 500 °C and 550 °C were analyzed. Raman spectrum of the pristine sample (Figure 9a) presents an intense Raman band at 870 cm^{-1} with a broad shoulder toward lower frequencies centered at about 820 cm^{-1} , and a weak shoulder toward higher frequencies at around 970 cm^{-1} . Two other Raman bands at lower frequencies (450 and 466 cm^{-1}), hardly resolved, are also observed. The profile of this spectrum is similar to those previously reported on these types of mixed oxide materials.⁵¹ The shoulder at 970 cm^{-1} can be assigned to stretching vibrations of terminal Mo=O and V=O bonds,⁵² whereas the bands appearing at the 770–880 cm^{-1} range have been associated to asymmetric Me–O–Me bridge stretching modes. The low frequency bands at around 470 cm^{-1} appear in a typical regime of their symmetric Me–O–Me bridge stretching modes. López Nieto et al.¹³ have shown that an intense Raman band at 874 cm^{-1} is present on both pure *M1* and *M2* phases, whereas Me–O–Me stretching modes are observed in both *M1* and *M2* crystalline phases. They assign bands located at 796 and 437 cm^{-1} to the *M2* phase, which are shifted to higher frequencies (827 and 470 cm^{-1}) in the case of the *M1* phase. Consequently as expected, Raman spectra of pristine catalyst allow identifying the presence of *M1* and *M2* crystalline phases in agreement with XRD spectra.

The comparison between pristine sample and the spent catalyst designated MoVNbO-S550 on the basis of corresponding Raman spectra, indicates significant differences especially in the low frequency Raman region. Raman spectrum of MoVNbO-S550 (Figure 10c) presents bands at the low frequency region clearly identified at 203, 228 280 and 340 cm^{-1} , which are associated to *M1* and *M2* phases. A more intense band toward higher frequencies located at 732 cm^{-1} is also observed. Notice that all these bands are more clearly detected in spent catalyst MoVNbO-S500

(vide Figure 9b) while in the case of the pristine catalyst they are practically not visible as illustrated in Figure 9a. M. Dieterle and G. Mestle⁵³ reported Raman bands of reduced monoclinic MoO₂ at 207, 230, 347, 364, 458, 496, 569, 585 and 740 cm⁻¹. The same assignation of bands was also reported by A. A. Bolzan et al.⁵⁴ The Raman bands at 744 and 589 cm⁻¹ have been attributed to the stretching vibrations of the Mo–O(I) and Mo–O(II) groups in the MoO₂ lattice. Thus, the Raman bands at 203, 228, 280, 340 and 732 cm⁻¹ clearly observed in MoVTeNbO-550S spent catalyst, are associated to monoclinic MoO₂ phase, which was segregated from *M1* or *M2* phases by effect of Te detachment from the intercalated framework channels of *M1* or *M2* phases under reaction conditions. The broad band at 458 cm⁻¹ come from an overlapping of 458 cm⁻¹ MoO₂ Raman band and the Raman bands of *M2* and *M1* phases centered at 450 and 466 cm⁻¹, respectively. In MoVTeNbO-550S spent catalyst, the stretching vibrations of the Mo–O(II) of the MoO₂ lattice was not observed, and the stretching vibrations of the Mo–O(I) groups shifts 12 cm⁻¹ to the lower frequencies. This may be explained in terms of the strong interaction between the different reduced molybdenum oxide species, which are being formed from progressive destruction of *M1* and *M2*, as suggested by HRTEM spectroscopy.

4. CONCLUSIONS

MoVTeNb mixed oxide is a highly active and selective catalyst for ODH-C₂ to ethylene, with a remarkable stability when operates at temperatures lower than 500 °C. The catalyst exhibited a conversion about of 50% with ethylene selectivity higher than 90% at T_{reaction}= 440 °C and space-time = 35 gcat h (mol ethane)⁻¹. Nevertheless the catalyst's stability is restricted to operate < 500°C, mostly due to a combination of reaction temperature and feed composition, in this case the inlet molar ratio C₂/O₂/N₂= 9/7/84. This result was unexpected, since the catalyst was previously activated by calcining at 600°C under N₂ flow, where an important amount of Te is

lost. Once reaction temperature is $\geq 500^\circ\text{C}$ brings about the removal of tellurium from the MoVTeNb mixed oxide catalysts, the loss of tellurium occurs preferentially from the ends parts of the *MI* crystal phase, across the [001] plane. Tellurium removal from the intercalated framework channels of *MI* phase brings about the partial destruction of MoVTeNb mixed oxide chiefly generating a MoO_2 crystalline phase and decreasing in consequence the catalyst's activity. The preservation of ethylene selectivity indicates that the catalytic sites remain unchanged, only a loss of them happens. Also none effect of MoO_2 crystalline phase over the ODH- C_2 reaction was observed. The detached tellurium from the MoVTeNb mixed oxide catalysts is carried out by means of a reduction process of Te^{4+} to Te^0 . Thus, hot spots along the reactor bed should be avoided or controlled in order to keep the catalytic bed temperature $< 500^\circ\text{C}$.

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Notes

The authors declare no competing financial interest.

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