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Additional Information

1 **Understanding the kinetic behavior of a Mo-V-Te-Nb mixed oxide in**
2 **the oxydehydrogenation of ethane**

3

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1 **Abstract**

2 Two kinetic models based on Langmuir-Hinshelwood (LH) and Eley-Rideal (ER)
3 mechanisms were developed to describe the oxydehydrogenation of ethane to yield ethylene over
4 a Mo-V-Te-Nb catalyst. Obtained in a lab-scale fixed-bed reactor, steady-state experimental data
5 were used to estimate the kinetic models parameters via a nonisothermal regression. Experiments
6 were performed using an ethane, oxygen and nitrogen mixture as feedstock, spanning
7 temperature from 673 to 753 K, inlet partial pressures of oxygen and ethane between 5.0 and 22.0
8 kPa, and space-time from 10 to 70 $\text{g}_{\text{cat}} \text{h}(\text{mol}_{\text{ethane}})^{-1}$. Ethylene, CO and CO₂ were the only
9 detected products, the selectivity for ethylene ranging from 76 to 96 % for an ethane conversion
10 interval 4-85 %. A series of tests feeding ethylene instead of ethane were also effectuated at 713
11 K, varying inlet partial pressures and space-time in the same ranges as did for ethane. Ethylene
12 conversion was relatively low, 3-14 %, the dominant product being CO with CO/CO₂ ratios from
13 0.73 to 0.79. The LH mechanism was found to represent better the experimental data. The
14 oxydehydrogenation of ethane was the reaction with the lowest activation energy, 108 - 115 kJ
15 mol^{-1} . Except for the conversion of ethane into CO₂, deep oxidations were detected as very
16 energetically demanding steps, 156 - 193 kJ mol^{-1} . Competitive adsorption between reagents and
17 products occurred in the two mechanisms particularly at relatively high reaction severity, water
18 re-adsorption being weaker in comparison with COx re-adsorption.

19

20

21 *Keywords: oxidative dehydrogenation; ethane; ethylene; Mo-V-Te-Nb catalyst; kinetics; Eley-*

22 *Rideal; Langmuir-Hinshelwood*

1 **1. Introduction**

2 Ethylene is, undoubtedly, the primary product in the petrochemical scenario [1]. Even
3 though the number of direct end-uses of ethylene is certainly limited, it is the base raw material
4 for manufacturing polymers, e.g., polyethylene, polystyrene and polyethylene chloride, together
5 with other important chemical compounds standing out ethylene oxide, ethanol and polyvinyl
6 acetate [2]. Worldwide, ethylene is mostly produced from the steam cracking of hydrocarbons [3]
7 and, to a lesser extent, via direct dehydrogenation of ethane in the presence or in the absence of
8 catalyst [4]. A common feature of these two processes is that they are performed at high
9 temperature (1025 K+) due to thermodynamic matters [5]. Evidently, high temperature operation
10 increases the installation costs as well as the operation expenses and, additionally, leads to a large
11 diversity of byproducts, a low ethylene yield and coke formation [6].

12 Focusing the attention on the Mexican scenario, ethylene is exclusively produced in ethane
13 crackers and used to a large extent to manufacture low density PE and high density PE, the
14 world's most extensively used plastic [7]. Statistics indicate that the local demand of PE
15 amounted to 1.6 millions of tons per year (MMTY) in 2005. In 2013, such a demand increased to
16 2.2 MMTY; notwithstanding, the existing PE manufacturers were capable to cover ca. 36 % of
17 the local demand. The efforts of the government to decrease the historical deficit of PE started
18 officially at the end of 2009 with the approval of the project "Etileno Siglo XXI" [7]. Evidently,
19 these actions will be accompanied by an enlargement of the production of ethylene.

20 Aimed at diversifying the options for producing ethylene and, at the same time, overcoming
21 inconveniences of the existing commercial processes outlined above, attention has been paid on
22 alternative processes [8]. Among them, the catalytic oxidative dehydrogenation (ODH) of ethane
23 is, undeniably, one of the most promising options. The ODH of ethane is an exothermic process

1 involving the reaction between ethane and an oxidant, usually oxygen [9]. Such a partial
2 oxidation process is, however, inevitably accompanied by the formation of CO and CO₂ (CO_x),
3 which is the result of very exothermic reactions. Apart from exhibiting the capacity to activate
4 the corresponding alkane at relatively low temperature, catalytic systems applied for the ODH of
5 ethane must display a remarkably high selectivity for ethylene, namely, reducing CO_x production
6 to a minimum level. Even though the list of catalysts historically used for the ODH of ethane is
7 extensive [10], [11], [12], [13], multimetallic mixed oxides containing Mo, Te, V and Nb are
8 reported as a very promising catalytic system in view of their high efficiency for producing
9 ethylene [10], [13].

10 The Mo-V-Te-Nb system is composed of two crystalline phases referred to as M1 and M2,
11 the former being the one containing the active/selective surface sites to activate ethane in partial
12 oxidation reactions. Phase M2 does not contain sites to activate ethane but is capable to catalyze
13 reactions involving olefins [14]. Some previous publications [13], [14] indicate that the Mo-V-
14 Te-Nb system starts to be active for the ODH of ethane below 573 K, namely, more than 450 K
15 below the value required by the existing commercial technologies. Besides leading to a
16 significant energy saving, lowering the operation temperature reduces the incidence of side
17 reactions and, hence, byproducts. An additional important challenge associated with the ODH of
18 ethane concerns with the reactor configuration due to the heat released by the chemical processes
19 referred above. Evidently, having reliable kinetic models at hands is a basic requirement for
20 performing reactor design, scale-up and optimization [16]. Kinetic models for the ODH of
21 ethane, which have been constructed on the basis of Power Laws (PL) empiricism as well as
22 Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen mechanisms [15], [17], [18], [19],
23 [20], [21], [22], [23] are already available in the literature. Nonetheless, such models are, strictly
24 speaking, only valid for the corresponding catalyst composition.

1 This work investigates on the catalytic performance of a Mo-V-Te-Nb catalyst for the ODH
2 of ethane combining experimental results with kinetics information. Lab-scale catalytic data were
3 collected at varying conditions of temperature, space-time as well as reactants (hydrocarbons and
4 oxygen) inlet partial pressure, and next used to estimate the parameters of two kinetic models
5 based on Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms. The ER model
6 assumes that the catalyst is composed of a single type of active site, whereas the LH one
7 considers there are two types of sites constituting the catalyst. In order to investigate on the
8 reactivity of the formed ethylene via the oxydehydrogenation of ethane, this alkene was used as
9 reagent in a selected number of experiments, which were also incorporated into kinetic
10 parameters estimation. The relative importance of the various steps occurring in the ODH of
11 ethane is finally assessed on the basis the kinetic models parameters.

12

13 **2. Experimental and procedures**

14 **2.1 Catalysts preparation**

15 The catalyst used in all the ODH experiments (vide infra) consisted of a multimetallic
16 mixed oxide containing Mo, V, Te and Nb, which was produced via the precipitation method.
17 This material was synthesized for a nominal atomic ratio of Mo:V:Te:Nb equal to
18 1:0.24:0.24:0.18. The following chemicals with corresponding purities reported by the suppliers
19 were used as main reagents during the catalyst's synthesis procedure, viz., Tetrahydrated
20 Ammonium Heptamolybdate 99 % (TAM) from Merck, Telluric Acid 98 % (TA) from Aldrich,
21 Ammonium Meta-Vanadate 99.5 % (AMV) from Sigma-Aldrich as well as Niobium Oxalate 99
22 % (NO) from ABCR Laboratories.

1 To produce the catalyst, an aqueous solution containing TAM, TA and AMV was prepared
2 at 353 K under continuous stirring. Separately a second aqueous solution containing NO and
3 oxalic acid (Aldrich, 98%) was prepared at 353 K. The second solution was added to the first one
4 maintaining a vigorous and continuous stirring to produce a slurry, which was then cooled to
5 room temperature. The slurry was acidified using an inorganic acid and later placed in a rotary
6 evaporator at 323 K and 27 kPa to eliminate progressively the water. The produced powder was
7 dried overnight at 373 K and finally subjected to a thermal treatment at 873 K for 2 h in a
8 nitrogen stream. More specific aspects concerning the catalyst preparation procedure along with a
9 series of important physicochemical properties of the resulting solid can be found elsewhere
10 [13],[15].

11

12 **2.2 Catalytic tests**

13 **2.2.1 Set-up**

14 To determine the catalytic performance of the Mo-V-Te-Nb catalyst, a series of ODH
15 experiments were effectuated in a semi-automatized lab-scale set-up. The feed section of this set-
16 up consisted of lines for ethane (99 % min purity), oxygen (99.9 % min purity) and nitrogen
17 (99.99 % min purity). In a selected set of experiments (vide infra), ethane was replaced by
18 ethylene, the latter contained in a mixture containing 50 vol.% ethylene in nitrogen. Aside from
19 diluting the reaction mixture directed to the reactor, nitrogen served as internal standard. Each
20 one of the feed lines mentioned above was equipped with a Brooks mod 5850I thermal mass flow
21 controller, which allows the quantification of the amount of gases directed to the reactor. The
22 reaction section of the set-up included a conventional fixed-bed reactor (FBR) that was made of a
23 quartz tube with an inner diameter of 1.0 cm. The FBR was operated at atmospheric pressure
24 feeding a mixture containing of ethane (or ethylene), oxygen and nitrogen. The sampling/analysis

1 section of the set-up comprised, as main component, an on-line HP-7890 series II Gases
2 Chromatograph (GC) that was equipped with FID and TCD detectors, in addition to an array of
3 three capillary columns. In agreement with the catalyst testing protocol, a first set of GC analyses
4 were performed to verify the composition of the reaction mixture before starting formally the
5 ODH reaction. A second series of GC analysis were next carried out to determine periodically the
6 composition of the reactor effluent after commencing the ODH reaction. The only carbon-
7 containing reaction products detected in the ODH experiments reacting ethane with oxygen, were
8 ethylene, CO as well as CO₂. When replacing ethane by ethylene in the reaction mixture directed
9 to the reactor, CO and CO₂ were the only reaction products. The water produced in different
10 chemical reactions taking place during the ODH feeding ethane and ethylene was indirectly
11 quantified by means of an oxygen balance.

12

13 **2.2.2 Reaction conditions**

14 The catalyst was sieved for an average particle size equal to 150 μm prior to be leaded into
15 the reactor. A constant mass of catalyst of 0.60 g was used in all tests. The experimental work
16 consisted in two blocks depending upon the fed hydrocarbon. In the first one, ethane was used as
17 hydrocarbon while the operating conditions were set to the following ranges: temperatures 673-
18 753 K, inlet partial pressures of oxygen and ethane 5.0-24.2 kPa, and space-times 10-70 g_{cat}
19 h(mol_{ethane})⁻¹. In the second series of tests, the experiments were carried out at 713 K, feeding
20 ethylene instead of ethane, varying inlet partial pressures of oxygen and ethylene as well as
21 space-times within the same ranges used in the experiments supplying ethane.

22 The carbon balances of the catalytic experiments situated within the range 100.0 % ± 2.0
23 %. Performed at the most severe reaction conditions, a couple of blank experiments demonstrated
24 that neither ethane nor ethylene was converted in the absence of catalyst. The FBR was operated

1 in the integral regime in accordance with the values of ethane conversion (vide infra). Likewise,
2 internal and external gradients at the particle scale, concerning concentration and temperature
3 were found to be below accepted limits [24], [25] and therefore, experimental observations were
4 obtained the so-called kinetic regime. Note that the catalytic responses values included in Section
5 3.1 are given on a carbon basis.

6

7 **2.3 Kinetic modeling**

8 The kinetic models to describe ODH of ethane developed in this work, vide infra, account
9 for 4 carbon-containing species, viz., ethane, ethylene, CO₂ and CO, as well as two noncarbon-
10 containing compounds corresponding to molecular oxygen and water. The global reactions
11 considered in each of these models amounts to five which, in particular, involve the combination
12 of ethane with oxygen to give (1) ethylene plus water, (2) CO₂ and water, and (3) CO plus water,
13 along with the reaction of ethylene and oxygen to produce (4) CO₂ and water, and (5) CO plus
14 water. The specific stoichiometry of each one of these reactions is represented by eqs. (1) to (5):



20

21 In accordance with a Power Law empiric kinetic expression, the rate of a reaction is
22 proportional to the partial pressure of the reagent(s) which, adapted to the i-th reaction involved
23 in the ODH of ethane, can be expressed by eq. (6):

1 $r_i = k_i P_{\text{HC}}^{\alpha_i} P_{\text{O}_2}^{\beta_i}$ (6)

2 In eq. (6), i is the subscript denoting the reaction in agreement with eqs. (1) to (5), k_i is the
3 corresponding rate coefficient, P is the partial pressure HC corresponding to ethane when $i=1, 2$
4 and 3, and ethylene when $i=4$ and 5, α_i is the reaction order associated to the partial pressure of
5 the hydrocarbon and β_i is the reaction orders relative to the partial pressure of oxygen. Since
6 some species can participate in more than one reaction, the net rate of production (or overall rate)
7 of the j -th species denoted as R_j has to be computed from the corresponding reaction rates and the
8 respective stoichiometric coefficients ($v_{j,i}$), as illustrated in eq. (7). Values of R_j are required in
9 the parameter estimation procedure, as will be explained further:

10 $R_j = \sum_{i=1}^{n_{\text{spec}}} v_{j,i} r_i$ (7)

11 Reaction orders are computed using experiments varying the inlet partial pressure of the
12 reagents. In the case of the O DH of ethane, the corresponding values are useful to determine
13 formally the manner the inlet partial pressure of oxygen and hydrocarbons (ethane and oxygen)
14 affect the reaction rates.

15

16 **2.3.1 Langmuir-Hinshelwood (LH) mechanism**

17 The LH mechanism considers that all reactants remain as adsorbed species over the catalyst
18 surface, on the active sites, before participating in any reaction, that sites are equivalent for
19 adsorption and that adsorbed molecules do not interact. The list of mechanism possibilities which
20 can be postulated is extensive accounting for the type(s) of active site(s) composing the catalyst,
21 the nature of the species adsorption (e.g., associative or dissociative), the rate determining step
22 (RDS), the option that products re-adsorb over the active sites competing with reagents, etc. The
23 results reported in a previous work [15] complemented with information presented in Section

1 3.1.3 relative to reaction orders, indicate that the adsorption of reagents, i.e. ethane (ethylene) as
2 well as oxygen, had to be discarded as RDS, i.e., corresponding reaction orders obtained from
3 experimental information displayed positive values. As diatomic molecules usually dissociate
4 directly upon adsorption, oxygen adsorption is considered to be dissociative. Besides, the option
5 for ethylene, water and CO_x re-adsorption is also incorporated into the mechanism since others
6 reported that these species may compete with the reagents for the active sites composing the
7 catalyst in oxidation reactions [23]. Some preliminary fitting work with simpler models was also
8 useful to postulate the LH mechanism finally outlined in this work.

9 Thus, incorporating into the modeling strategy what was mentioned in the previous
10 paragraph, the LH mechanism was ultimately constructed in accordance with the next specific
11 assumptions: (i) the catalyst consists of two types of active sites designated S₁ and S₂, (ii)
12 associative hydrocarbons (ethane and ethylene) adsorption occurs over sites S₁ and dissociative
13 oxygen adsorption takes place over sites S₂, (iii) surface reactions are considered as rate
14 determining steps, all of them involving adsorbed hydrocarbons and adsorbed oxygen to yield
15 ethylene, CO₂, CO and water; (iv) all these products can be re-adsorbed over the two types of
16 active sites, in particular, ethylene over the sites S₁, and CO_x as well as water over the sites S₂.
17 The (re-)adsorption of species is assumed to be quasi-equilibrated with the gas phase. Also using
18 reaction data over the Mo-V-Te-Nb catalytic system, others [26] developed a two sites LH
19 mechanism to describe the partial oxidation of propane to acrylic acid.

20

21

Table 1 is displayed here.

22

23

24

Table 1 presents the elementary steps that were accounted for in LH mechanism. Steps *a*
and *b* represent the adsorption of the two reagents, ethane and oxygen, while steps *c*, *d*, *e* and *f*

1 are used to denote the re-adsorption of products, ethylene, CO₂, CO and water, respectively.
 2 Numbers 1 to 5 are used to denote the surface reactions, more particularly, reaction 1, 2 and 3
 3 involves adsorbed ethane and adsorbed oxygen to give adsorbed ethylene and adsorbed water,
 4 adsorbed CO₂ and adsorbed water, and adsorbed CO and adsorbed water, respectively.
 5 Additionally, numbers 4 and 5 represent the reaction between adsorbed ethylene and adsorbed
 6 oxygen to produce adsorbed CO₂ and adsorbed water, as well as adsorbed CO and adsorbed
 7 water, respectively. Notice that as proposed by others [20],[23],[29] in oxidation studies, the
 8 activation of the adsorbed hydrocarbon with adsorbed oxygen is considered as the rate
 9 determining step in all these five reactions.

10 The rate expression for the i-th surface reaction (vide Table 1) is, thus, given by eq. (8):

$$11 \quad r_i = k_i \Theta_{\text{HC}} \Theta_{\text{O}_2} \quad (8)$$

12 In eq. (8), k_i is the rate coefficient, θ_{O_2} is the fraction of sites occupied by oxygen, θ_{HC} is the
 13 fractional site coverage of hydrocarbons, the subscript HC standing for ethane when $i=1, 2$ and 3 ,
 14 and ethylene when $i=4$ and 5 .

15 For the steps in quasi-equilibrium, the use of the Langmuir concepts allows the calculation
 16 of the fraction of sites occupied by the corresponding adsorbed species. Recall that a two sites
 17 balance needs to be performed. In the case of the sites type S_1 , the fraction of active sites
 18 occupied by ethane and ethylene corresponds to eqs. (9) and (10), respectively, and involves the
 19 partial pressure of the respective hydrocarbon:

$$20 \quad \Theta_{\text{C}_2\text{H}_6} = K_{\text{C}_2\text{H}_6} P_{\text{C}_2\text{H}_6} \Theta_{\text{S}_1} \quad (9)$$

$$21 \quad \Theta_{\text{C}_2\text{H}_4} = K_{\text{C}_2\text{H}_4} P_{\text{C}_2\text{H}_4} \Theta_{\text{S}_1} \quad (10)$$

22 In eqs. (9) and (10), $K_{\text{C}_2\text{H}_6}$ and $K_{\text{C}_2\text{H}_4}$ are the adsorption coefficient for ethane and ethylene
 23 respectively, while θ_{S_1} represents the fraction of unoccupied active sites type 1. Having in mind

1 that the number of each type of site remains constant, the sites balance of for the case of the sites
 2 type S_1 is represented by eq. (11):

$$3 \quad 1 = \Theta_{S_1} + \Theta_{C_2H_6} + \Theta_{C_2H_4} \quad (11)$$

4 Substituting eqs. (9)-(10) in eq. (11) and implementing some simplifications, the fraction of
 5 empty sites type S_1 were finally computed by means of eq. (12):

$$6 \quad \Theta_{S_1} = \frac{1}{1 + K_{C_2H_6} P_{C_2H_6} + K_{C_2H_4} P_{C_2H_4}} \quad (12)$$

7 Analogously, the fraction of free sites type S_2 can be expressed in terms of eq. (13)
 8 considering that oxygen along with water and CO_x are the species that can accommodate over
 9 this type of sites:

$$10 \quad \Theta_{S_2} = \frac{1}{1 + \sqrt{(K_{O_2} P_{O_2} + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O})}} \quad (13)$$

11 Finally, the explicit form of the rate equation of the i -th reaction (vide Table 1) adopts the
 12 form of eq. (14):

$$13 \quad r_i = \frac{k_i (K_{HC} P_{HC}) \sqrt{K_{O_2} P_{O_2}}}{[1 + K_{C_2H_6} P_{C_2H_6} + K_{C_2H_4} P_{C_2H_4}] [1 + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2} + K_{H_2O} P_{H_2O}}]} \quad (14)$$

14 In eq. (14), the subscript HC holds for ethane when $i=1, 2$ and 3 , and ethylene for $i=4$ and
 15 5 . The net rate of production of the j -th species was ultimately computed with eq. (7).

16

17 **2.3.2 Eley-Rideal (ER) mechanism**

18 In the Eley-Rideal mechanism, by definition, one of the reagents reacts directly from the
 19 gas phase with another one on the surface. In similar manner as described above for the LH
 20 mechanism, a set of assumptions were made in order to develop the ER mechanism for the ODH
 21 of ethane. More precisely, it is first assumed that the catalyst is composed of a single type of
 22 active site denoted as S . Dissociative adsorption of the gas oxygen also occurs over this type of

1 sites. Five surface reactions are accounted for in which, adsorbed oxygen reacts with gas phase
2 hydrocarbons to produce ethylene, CO₂ and CO, vide Table 2. It was, additionally, assumed that
3 except for ethylene all formed product are susceptible to be re-adsorbed over the sites of the
4 catalyst. (Re-)adsorption steps are assumed to be quasi-equilibrated.

5 Table 2 shows the set of elementary steps taken into consideration for developing the ER
6 kinetic model. Step *a* represent the dissociative adsorption of oxygen, while stages *b*, *c* and *d* are
7 used to denote the re-adsorption of products CO₂, CO and water, respectively. The steps labeled
8 with numbers 1 to 5 correspond to the surface reactions mentioned above. In the steps denoted by
9 1, 2 and 3, gas phase ethane and adsorbed oxygen react to give gas phase ethylene and adsorbed
10 water, adsorbed CO₂ and adsorbed water, as well as adsorbed CO and adsorbed water,
11 respectively. Besides, steps 4 and 5 represent the reaction between gas phase ethylene and
12 adsorbed oxygen to produce adsorbed CO₂ and adsorbed water, as well as adsorbed CO and
13 adsorbed water, respectively. In all these reactions, the activation of the gas phase hydrocarbon
14 with adsorbed oxygen is considered as the rate determining step in these five reactions.

15 In accordance with the statements given, the rate expression for the *i*-th surface reaction
16 (vide Table 2) is given by eq. (15):

$$17 \quad r_i = k_i P_{HC} \theta_{O_2} \quad (15)$$

18 In eq. (15), k_i is the rate coefficient of the *i*-th reaction, P_{HC} is the hydrocarbon partial
19 pressure HC denoting ethane when $i=1, 2$ and 3, and ethylene for $i=4$ and 5, while θ_{O_2} is the
20 fraction of sites occupied by oxygen.

21 Except for ethane and ethylene which react from the gas phase, all the other species are
22 assumed to be adsorbed over the catalyst's sites. Hence, after using the quasi-equilibrium

1 approximation during the (re-)adsorption steps, the fraction of sites occupied by the different
 2 species (Θ_i) can be computed by applying eqs. (16)-(19):

$$3 \quad \Theta_{O_2} = \Theta_S \sqrt{K_{O_2} P_{O_2}} \quad (16)$$

$$4 \quad \Theta_{CO_2} = K_{CO_2} P_{CO_2} \Theta_S \quad (17)$$

$$5 \quad \Theta_{CO} = K_{CO} P_{CO} \Theta_S \quad (18)$$

$$6 \quad \Theta_{H_2O} = K_{H_2O} P_{H_2O} \Theta_S \quad (19)$$

7 As was also indicated in Section 2.3.1., the application of the principle of sites conservation
 8 considering the total number of sites is constant, results in eq. (20), θ_S denoting the fraction of
 9 unoccupied active sites:

$$10 \quad 1 = \Theta_S + \Theta_{O_2} + \Theta_{H_2O} + \Theta_{CO_2} + \Theta_{CO} \quad (20)$$

11 The combination of eqs. (16)-(19) with eq. (20) results in eq. (21), corresponding to an
 12 explicit expression to compute the value of θ_S :

$$13 \quad \Theta_S = \frac{1}{1 + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O}} \quad (21)$$

14

15 **Table 2 is displayed here.**

16

17 For the i-th reaction, in agreement with what is displayed in Table 2, the explicit expression
 18 of the corresponding rate equation results in eq. (22):

$$19 \quad r_i = \frac{k_i P_{HC} \sqrt{K_{O_2} P_{O_2}}}{1 + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O}} \quad (22)$$

20 In eq. (22), when $i=1, 2$ and 3 the subscript HC corresponds to ethane, and for $i=4$ and 5
 21 HC denotes ethylene. Using eq. (7) allows the calculation of the net rate of production of the j-th
 22 species.

23

1 2.3.3 Parameters estimation

2 The temperature dependence of the rate coefficients is represented by the Arrhenius
3 equation which, for a reaction i , includes two parameters, namely, an activation energy (E_i) and a
4 pre-exponential factor (A_i), as observed in eq. (23):

$$5 \quad k_i = A_i \exp\left(\frac{-E_i}{RT}\right) \quad (23)$$

6 To determine directly the effect of temperature on the values of the rate coefficients, a
7 parameters estimation using simultaneously the experimental data at different temperatures was
8 performed. Such a parameters estimation procedure gives values of activation energies and pre-
9 exponential factors with corresponding individual statistics. Since pre-exponential factors and
10 activation energies are usually correlated, it is a convenient practice to use pre-exponential
11 factors in the so-called reparameterized form. Consequently, the rate coefficient of a reaction i
12 can be alternatively computed using the reparameterized Arrhenius expression, vide eq. (24):

$$13 \quad k_i = A_{\text{rep},i} \exp\left(\frac{E_i}{R} \left[\frac{1}{T_m} - \frac{1}{T}\right]\right) \quad (24)$$

14 The reparameterized pre-exponential factor represented by $A_{\text{rep},i}$ is calculated with eq. (25),
15 corresponding to an expression that incorporates a mean temperature value denoted as T_m . Notice
16 that the values of $A_{\text{rep},i}$ correspond to the rate coefficient of reaction i computed at T_m :

$$17 \quad A_{\text{rep},i} = A_i \exp\left(-\frac{E_i}{RT_m}\right) \quad (25)$$

18 The adsorption coefficients designated K_j j corresponding to a given species, are treated in
19 a similar way as done for rate coefficients as their values changes with temperature as well. The
20 temperature dependence of K_j is given by the Van't Hoff expression that includes a standard
21 entropy of adsorption (ΔS_j°) and a standard enthalpy of adsorption (ΔH_j°), vide eq. (26).

$$22 \quad K_j = \exp\left(\frac{\Delta S_j^\circ}{R} - \frac{\Delta H_j^\circ}{RT}\right) \quad (26)$$

1 In order to avoid the strong correlation between the two adsorption parameters accounted
 2 for in eq. (28), the Van't Hoff expression is also used in the reparameterized form represented by
 3 eq. (27):

$$4 \quad K_j = \Delta S_{\text{rep},j}^{\circ} \exp\left(\frac{\Delta H_j^{\circ}}{R} \left[\frac{1}{T_m} - \frac{1}{T}\right]\right) \quad (27)$$

5 $\Delta S_{\text{rep},j}^{\circ}$ is the reparameterized standard adsorption entropy of component j , which can be
 6 computed by applying eq. (28). The values of $\Delta S_{\text{rep},j}^{\circ}$, in fact, correspond to the adsorption
 7 coefficients of the j -th species evaluated at T_m :

$$8 \quad \Delta S_{\text{rep},j}^{\circ} = \exp\left(\frac{\Delta S_j^{\circ}}{R} - \frac{\Delta H_j^{\circ}}{RT_m}\right) \quad (28)$$

9 An additional issue addressed during the parameters estimation procedure was related to
 10 statistics. On this respect, the capacity of the models to represent the experimental data, namely,
 11 the model adequacy was assessed by means of the F-test. For each estimated parameter, the
 12 corresponding confidence region was computed on the basis of the t-test at the 95 % probability.
 13 Finally, parity plots were also constructed so as to visualize the agreement between experimental
 14 observations and models predictions.

15 The estimation of the kinetic parameters was performed by minimizing an objective
 16 function represented by eq. (29) that includes the weighted sum of squares of the residuals (RSS)
 17 between yields predicted by the model ($\hat{Y}_{i,j}$) and experimental molar yields ($Y_{i,j}$) for the species
 18 involved in the reactions represented by eqs. (1) to (5):

$$19 \quad \text{RSS}(\beta) = \sum_{i=1}^{n_{\text{obs}}} \sum_{j=1}^{n_{\text{resp}}} w_j (Y_{i,j} - \hat{Y}_{i,j})^2 \xrightarrow{\beta_1, \beta_2, \dots} \min \quad (29)$$

20 In eq. (29), β is the vector of kinetic parameters to be estimated via regression, n_{obs} is the
 21 number of independent experiments, n_{resp} is the number of responses, while w_j is a weight factor
 22 that is commonly used for tuning the relative importance of the various responses. For an

1 experiment i , the experimental molar yield of a species j is calculated by means of eq. (30), that
2 involves molar flow rates:

$$3 \quad Y_{i,j} = \frac{F_{i,j}}{F_{i,\text{hydrocarbon}}^0} \times 100 \quad (30)$$

4 Predicted yields included in the objective function were obtained via numerical integration
5 of the corresponding reactor model equations, which are given in terms of a set of ordinary
6 differential equations (ODEs), vide eq. (31):

$$7 \quad R_{i,j} = \frac{d\hat{Y}_{i,j}}{d(W/F_{\text{hydrocarbon}}^0)_i} \quad (31)$$

8 For the i -th experiment, the net rate of formation of species j represented by $R_{i,j}$ which can
9 be computed applying eq. (7), vide supra. The boundary condition for experiment i and species is
10 given by $Y_{i,j}(0) = 0.0$.

11 The set of ODEs given by eq. (31) stands for a continuous pseudo-homogeneous,
12 isothermal, isobaric one-dimensional plug flow reactor, which is operated in the integral regime,
13 in the absence of concentration and thermal gradients at the pellet scale. The integration of ODEs
14 was performed numerically incorporating the LSODA routine [27].

15 ODRPACK 2.01 solver [28] was used to obtain the parameters that minimize the objective
16 function, vide eq. (14), via nonlinear ordinary least squares for explicit models with an
17 implementation of the Levenberg-Marquardt algorithm.

18

1 **3. Results and discussion**

2 **3.1 Experimental results**

3 **3.1.1 ODH of ethane**

4 In the case of the ODH experiments feeding ethane, ethylene was identified as the main
5 reaction product. CO_x were also detected, the amount CO produced during the reaction being
6 systematically larger than that of CO₂. The specific relative contribution of each product to the
7 reactor effluent was found to be influenced by the specific reaction conditions, i.e., temperature,
8 space-time and reagents inlet partial pressures. Figure 1 displays the progress of the yields to
9 ethylene, CO and CO₂ as well as the conversion of oxygen as a function of ethane conversion, for
10 a set of experiments varying simultaneously temperature from 673 – 753 K, and space-time
11 between 22 and 70 g_{cat} h(mol_{ethane})⁻¹, at a given feedstock composition. Evidently, the production
12 of ethylene, CO and CO₂ along with the conversion of oxygen increases nonlinearly with ethane
13 conversion. More precisely, the slopes of the ethylene yield curve decrease and the slopes of the
14 CO_x curves increase with ethane conversion, thus indicating a decline in the relative contribution
15 of ethylene to the total products as more ethane is consumed in the reaction. A higher production
16 of CO_x implies a larger consumption of oxygen in accordance with the stoichiometry of the
17 corresponding reactions, vide eqs. (1) to (5). In a previous publication [15], the concomitant
18 effect of temperature and space-time on a set of catalytic responses during the ODH of ethane
19 over the same Mo-V-Te-Nb mixed oxide was assessed in detail. Briefly, moving into the high
20 reaction severity region, namely, increasing temperature and/or space-time, has a positive effect
21 on ethane conversion and CO_x selectivity in detriment to the selectivity to ethylene. After
22 combining the yields with the conversions of Figure 1, the highest ethylene selectivity amounted
23 96 % and the lowest 76 % corresponding, respectively, to ethane conversions of 16 and 86 %.

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Figure 1 is displayed here.

Figure 2 includes the plots of the yields to ethylene and CO_x as a function of the inlet partial pressure of ethane, whilst Figure 3 displays plots of the yields to ethylene and CO_x as a function of the inlet partial pressure of oxygen. Clearly, increasing the inlet partial pressures of ethane and/or oxygen has a positive effect on the yield to products due to a more vigorous conversion of the reagents. From a more detailed inspection of Figures 2 and 3, it is evident that the yields to ethylene and CO_x are appreciably more sensitive to changes in the inlet partial pressure of ethane than they are to changes in the inlet partial pressure of oxygen. At a space-time of 35 g_{cat} h(mol_{ethane})⁻¹, for instance, augmenting the inlet partial pressure of ethane from 5 to 22 kPa duplicates from 28 to 58 % the yield to ethylene (Figure 2a), whereas when the inlet partial pressure of oxygen is varied within the same range the yield to ethylene only augments from 37 to 42 % (Figure 3a). Also, the positive effect of increasing the inlet partial pressure of oxygen appears to be less evident in the case of the yield to ethylene compared with that to CO_x. In order to assess formally the inlet partial pressure effect on the reaction rates and the catalytic responses, partial reaction orders related to ethane and oxygen were computed by combining the available experimental with eq. (6). The corresponding results are outlined and discussed with some detail further in Section 3.1.3.

Figure 2 is displayed here

Figure 3 is displayed here

1 **3.1.2 ODH with ethylene**

2 The experimental results of the ODH reaction feeding ethylene instead of ethane
3 demonstrated that the Mo-V-Te-Nb catalyst is also capable to activate ethylene conversion albeit
4 to a lesser extent than ethane. Ethylene exhibited a relatively low reactivity yielding only
5 oxidation products, i.e., CO and CO₂, the former being the dominant species. At the reaction
6 conditions specified in Section 2.2.2, from 3 to 14 % of the fed ethylene was converted, the yield
7 to CO ranged 6 - 21% while the ratio CO to CO₂ varied between 2.7 and 3.7 (Figure 4). The ratio
8 CO to CO₂ was found to slightly decrease with ethylene conversion.

9

10 **Figure 4 is displayed here**

11

12 The effect of varying ethylene and oxygen inlet partial pressures on the yields to CO_x was
13 also investigated. On the basis of the plots Figure 5 which only include the CO profiles for
14 brevity's sake, it is observed that augmenting the inlet partial pressure of ethylene and/or oxygen
15 leads to larger values of CO yields as a consequence of a more vigorous conversion of ethylene.
16 In agreement with what was observed above for the ODH experiments feeding ethane, the yield
17 to CO is appreciably more sensitive to changes in ethylene inlet partial pressure than it is to
18 variations in the oxygen inlet partial pressure. For example, at a space-time of 35 g_{cat} h
19 (mol_{ethylene})⁻¹ by increasing the inlet partial pressure of ethylene from 5 to 22 kPa, the yield to CO
20 practically triplicates from 8 to 25 % (Figure 5a), whereas when the inlet partial pressure of
21 oxygen is varied within the same range the yield to ethylene only augments from 12 to 15 %
22 (Figure 5b). Partial reaction orders related to ethylene and oxygen were also calculated, vide
23 Section 3.1.3.

24

1 **Figure 5 is displayed here**

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3 The experimental results of the ODH feeding ethylene were combined with those of the
4 ODH of ethane in order to approximate the contribution of ethane and ethylene to the total
5 oxidation products (CO_x) finally observed in the ODH of ethane. From a carbon balance of the
6 catalytic tests performed at 713 K, space-times 22 – 70 g_{cat} h (mol_{hydrocarbon})⁻¹, oxygen inlet partial
7 pressures between 5.0 and 22.0 kPa, and an ethane inlet partial pressure of 11.0 kPa, it was
8 demonstrated that CO and CO₂ are also produced out of ethane. The CO to CO₂ ratio varied from
9 1.5 to 2.0 and, hence, it is clear that ethane conversion is less selective to CO than ethylene
10 conversion is. A more detailed assessment of the experimental results was made to quantify the
11 contribution of the CO coming from the ethylene reconversion to the total amount of CO
12 observed in the ODH of ethane. Figure 6 contains a graph showing the percentage of CO coming
13 from ethylene (%CO from ethylene) relative to the total CO produced in the ODH of ethane as a
14 function of the inlet partial pressure of oxygen at three different values of space-time. Note that
15 the amount of CO (as %CO) from ethylene increases with space-time but, decreases as the inlet
16 partial pressure of oxygen augments. The contribution of the ethylene reconversion to the total
17 oxidation appears to be particularly sensitive to changes in the space-time. Operating at larger
18 values of space-time leads to a higher production of ethylene and, therefore, a larger amount of
19 the olefin is available to produce CO_x. Actually, within the experimental region outlined above,
20 ethylene contributes from ca. 50–90 % of the total CO produced during the ODH of ethane
21 experiments, the largest value detected at the most severe reaction conditions.

22

23 **Figure 6 is displayed here**

24

1 **3.1.3 Partial reaction orders**

2 To quantify formally the effect of the oxygen and hydrocarbon (ethane and ethylene) partial
3 pressure on the catalyst performance, the respective reaction orders were computed in accordance
4 with the procedure outlined in ref. [29], [30]. For this end, the experiments at a constant ethane
5 (and ethylene) and oxygen partial pressure were used, vide Section 2.2.2 for the specific reaction
6 conditions. Since two reagents are involved in all the reactions, vide eqs. (1)–(5) and (6), two
7 partial reaction orders per reaction had to be calculated. Computed out of the ODH of ethane
8 experiments, partial reaction orders associated to the reactions represented by eqs. (1) to (3),
9 were, respectively, 1.46, 1.61 and 1.76 for ethane, as well as 0.17, 0.36 and 0.43 for oxygen.
10 Aside, the partial reaction orders related to eqs. (4) and (5) were obtained using the ODH data
11 feeding ethylene information amounting, respectively, to 1.11 and 1.04 for ethylene, as well as
12 0.21 and 0.29 for oxygen. These results are in accordance with what was qualitatively commented in
13 Sections 3.1.1 and 3.1.2., concerning the dependence of the catalyst performance on the
14 hydrocarbons and oxygen partial pressures. Note that the oxydehydrogenation of ethane to
15 ethylene corresponding to eq. (1) exhibited the lowest reaction order related to oxygen. For the
16 reactions producing CO_x, additionally, it is inferred from the corresponding values of the reaction
17 orders that ethane conversion appears to be more sensitive to changes in the hydrocarbon partial
18 pressure than ethylene conversion is; a situation that is, in turn, opposite to what was observed for
19 the oxygen partial pressure.

20

21 **3.2 Kinetics modeling**

22 **3.2.1 LH mechanism**

23 From a nonisothermal regression of the steady-state experimental data (vide Section 2.2.2
24 for the specific reaction conditions), the kinetic parameters associated to the Arrhenius and Van't

1 Hoff expressions, eqs. (24) and (27) respectively, were estimated simultaneously. On the basis of
2 the F-tests of the global regression results, the model represents adequately the experimental data
3 as the computed F-value was 1981, while the tabulated one amounted to 2.79. Figure 7 includes
4 the so-called parity diagrams which, in the case of this work, confront molar yields predicted by
5 the model with molar yields obtained via experiments. It is observed that the model describes
6 reasonably well the experimental data.

7 Table 3 displays main values of activation energies and reparameterized pre-exponential
8 factors with corresponding 95% probability confidence limits. On account of the later, all these
9 parameters were found to be statistically significant. Main values of activation energy lie within
10 the range 114.9 to 190.0 kJ (mol)⁻¹. The oxydehydrogenation of ethane to yield ethylene is the
11 reaction with the lowest activation energy, 114.9 ± 5.8 kJ (mol)⁻¹. On the contrary, the formation
12 CO₂ via the total oxidation of ethylene is the reaction with the largest energy barrier to take place,
13 190.0 ± 5.8 kJ (mol)⁻¹. Among the reactions responsible for CO_x production, the total oxidation
14 of ethane leading to CO₂ appears to be the step with the smallest demand of energy to occur,
15 122.7 ± 16.6 kJ (mol)⁻¹. Considering that as temperature augments so does the relative
16 importance of reactions with larger activation energies, the trend of this set of model parameters
17 is in agreement with the increment in the relative contribution of CO_x to the total products as a
18 result of a higher temperature operation, vide Section 3.1.1.

19 The pre-exponential factors of the different reactions accounted for in the kinetic model are
20 also depicted in Table 3. They range from around 10⁴ to 10¹⁰ mol(g_{cat} h kPa)⁻¹ the largest values
21 corresponding to deep oxidation reactions involving ethylene, which also exhibited the highest
22 activation energies as shown above. In the case of LH mechanisms, these large pre-exponential
23 factors are characteristic of surface species with a low mobility [31]. Additionally, an assessment
24 of the main values of the reparameterized pre-exponential factors displayed in Table 3 is useful to

1 compare the magnitude of the rate coefficient of the various reactions at the mean temperature,
2 $T_m=713$ K, vide eqs. (24) and (25). At these conditions, the rate coefficient of the
3 oxydehydrogenation of ethane to produce ethylene is, for instance, one order of magnitude larger
4 than that of the formation of CO out of ethylene, two orders of magnitude higher than that of the
5 production of CO₂ from ethane and eight orders of magnitude larger than that of the production
6 of CO from ethane. On the basis of these results, the transformation of ethane to ethylene is the
7 fastest reaction and the conversion of ethane to CO the slowest one. Differences in rate
8 coefficients may be, however, partially compensated by changes in partial pressures.

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Table 4 is displayed here.

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12 As far as the Van't Hoff's equation parameters, also included in Table 3, is concerned,
13 estimated standard adsorption enthalpies along with reparameterized standard adsorption
14 entropies were also statistically significant. Both standard adsorption enthalpy and entropy
15 exhibit physical consistency considering the set of criteria proposed by Boudart et al. [32]. More
16 specifically, estimated standard adsorption enthalpies are all negative corresponding to
17 exothermic processes, whereas the standard adsorption entropies systematically situate within -
18 $41.8 \text{ J (mol K)}^{-1}$ and the respective gas phase molecular standard entropy. The fact that all
19 standard adsorption enthalpies are all negative means that the corresponding adsorption
20 coefficients decrease with temperature, such a negative effect being more pronounced as the
21 absolute value of ΔH_j^0 augments. Over sites type 1, the standard adsorption enthalpy of ethylene
22 is more negative than that of ethane, $- 64.0 \pm 9.0 \text{ kJ (mol)}^{-1}$ vs $- 21.5 \pm 5.9 \text{ kJ (mol)}^{-1}$, suggesting
23 a stronger chemisorption of the olefin. Over sites type 2, the adsorption of water is the least
24 exothermic process $- 20.7 \pm 4.6 \text{ kJ (mol)}^{-1}$, while the largest correspond to CO_x adsorption, i.e. -

1 $80.3 \pm 20.0 \text{ kJ (mol)}^{-1}$ for CO_2 and $- 80.3 \pm 27.8$ for CO . From these results, it is suspected that
2 products re-adsorption, i.e., ethylene in the case of sites type 1, and CO_x as well as water in the
3 case of sites type 2, may compete with the corresponding reagents, ethane and oxygen,
4 respectively, for available free sites.

5 The final value of the adsorption coefficient of a given species, however, accounts for the
6 contribution of the standard adsorption enthalpy and the adsorption entropy. ΔS° is related to the
7 decrease in freedom of motion of the species during adsorption; in fact, such a loss of augments
8 as the absolute value of ΔS° increases. Over sites type 2, the most negative values of ΔS°
9 denoting the largest entropy loss, are exhibited by CO_2 and CO adsorption, $- 137.4$ and $- 116.7 \text{ J}$
10 $(\text{mol K})^{-1}$, respectively, these two process corresponding to the most exothermic ones as
11 discussed above. Large absolute values of ΔH° are usually accompanied by high absolute values
12 of ΔS° , a behavior that is also detected in the case of the adsorption parameters related to site
13 type 1 (vide Table 3) and reported by others [33].

14 The reparameterized standard adsorption entropy corresponds to the adsorption coefficients
15 computed at the mean temperature, T_m in eqs. (23) and (24). At a given partial pressure, the
16 higher the adsorption coefficient of a species is, the larger the surface coverage is expected.
17 Concerning sites type 1, the information in Table 1 indicates the adsorption coefficient of ethane
18 is just slightly larger than that of ethylene. Related to sites type 2, oxygen exhibited the largest
19 adsorption coefficient, which is two orders of magnitude higher than the one displayed by CO ,
20 and three orders of magnitude larger than that exhibited by water. This indicates that, in principle,
21 products re-adsorption evolves as follows: $\text{CO} > \text{CO}_2 \gg \text{water}$, while it seems that re-adsorbed
22 CO_x does compete with oxygen for sites during the progress of the reaction. Recall that apart
23 from being influenced by the adsorption parameters outlined above, the fractional site coverage

1 of a given species is affected by the partial pressure and temperature, which depend on the
2 particular reaction conditions. Thus, the observed differences in the magnitude of the adsorption
3 coefficient may be partially compensated by changes in partial pressures.

4
5 **Figure 7 is displayed here.**
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7 **3.2.2 ER mechanism**

8 In accordance with the F-test, this model also reproduces adequately the experimental
9 observations exhibiting a computed F-value for the global significance of the regression equal to
10 1098. This value is much larger compared with the tabulated one (2.79) albeit appreciably lower
11 in comparison with the one obtained for the LH model above (F-value= 1981). The information
12 from the F-test combined with the parity plots included in Figure 8 for the ER model, indicates
13 that the LH model represents better the experimental data used in parameters estimation
14 procedure.

15 Table 4 depicts the main values as well as 95 % confidence limits of activation energies,
16 reparameterized pre-exponential factors, standard adsorption enthalpies and with reparameterized
17 standard adsorption entropies. None of the individual confidence intervals include zero, and
18 hence, all estimates exhibited statistical significance. Main values of activation energy belong to
19 the interval 108.2 – 193.4 kJ (mol)⁻¹. In agreement with what was obtained for the LH model, the
20 ER model reports that the oxydehydrogenation of ethane to yield ethylene is the reaction with the
21 lowest activation energy, 108.2 ± 8.8 kJ (mol)⁻¹. As also observed with the LH model, the
22 activation energies of the ER model indicate the transformations of ethylene to total oxidation
23 products are the most energetically demanding steps among the five reactions accounted for in
24 the model. The transformation of ethane to CO₂ is the chemical process with the smallest

1 activation energy considering the reactions of deep oxidation, i.e., $156.5 \pm 30.2 \text{ kJ (mol)}^{-1}$. In
2 accordance with the activation energy values, this model also appears to represent well the
3 temperature effect on products distribution, for instance, the increase in the relative importance of
4 ethylene formation relative to the oxidation products at low temperature operation. As also
5 detected with the LH model, the pre-exponential factors the reactions involving ethylene
6 oxidation are the largest, ca. $10^9 \text{ mol (g}_{\text{cat}} \text{ h kPa)}^{-1}$, as depicted in Table 4. Large values of pre-
7 exponential factors are frequently associated to reactions with high activation energies in which,
8 corresponding activated complexes exhibit a relatively simple. Such an activated complexes in
9 the particular case of ER mechanisms, display a high mobility [31][34].

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Table 5 is displayed here.

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Figure 8 is displayed here.

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15 Related to the Van't Hoff's expression parameters reported in Table 4, physical consistency
16 is also observed in agreement with the criteria mentioned in the previous section. Likewise, the
17 adsorption of CO is the most exothermic process, $-137.5 \pm 46.7 \text{ kJ (mol)}^{-1}$, and the adsorption of
18 oxygen one is the least one, $-38.1 \pm 7.4 \text{ kJ (mol)}^{-1}$. Water is less strongly adsorbed, -38.1 ± 7.4
19 kJ (mol)^{-1} , over the catalyst sites compared with COx. These results suggest that products
20 compete with oxygen for the available active sites and, consistently with what was found for the
21 LH mechanism, COx species re-adsorb more strongly over the catalyst compared with water. The
22 most negative value of ΔS° is exhibited by CO adsorption, $-197.1 \text{ J (mol K)}^{-1}$ corresponding as
23 indicated above, to the most exothermic adsorption. Such an enthalpy-entropy compensation
24 effect was also observed in the model LH, vide supra. In fact, when plotting the values of ΔS°

1 and ΔH° associated to the LH and ER models developed in this work, a linear correlation is
2 observed, vide Figure 9.

3 The values of the reparameterized standard adsorption entropies displayed in Table 4
4 indicate that, at $T_m = 713$ K, the adsorption coefficients of CO_2 and oxygen are one order of
5 magnitude higher than that of CO and four orders of magnitude larger compared with that of
6 water. As also detected with the LH mechanism, the ER model results indicate that the inhibition
7 effect of water on the oxygen adsorption is unimportant contrary to what occurs with CO_x .

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Figure 9 is displayed here.

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11 **4. Conclusions**

12 The performance of a Mo-V-Te-Nb catalyst for the ODH of ethane was investigated
13 applying experimental and modeling tools. Experiments were performed under varying
14 conditions of temperature, space-time, and inlet partial pressure of ethane and oxygen. Increasing
15 reaction severity leads to higher ethane conversions and a higher selectivity to CO_x in detriment
16 to that of ethylene. A selected set of tests feeding ethylene instead of ethane demonstrated that
17 ethylene is a primary nonstable product leading to CO as a dominant product, and that CO_x are
18 formed out of both ethane and ethylene. Even though ethylene is not very reactive at the ODH
19 conditions, its contribution to the deep oxidation products may be very important during the
20 ODH of ethane, in particular, when increasing reaction severity operation. Ethane and ethylene
21 conversions and respective products distribution were found to be less sensitive to changes in the
22 oxygen partial pressures than they are to variations in the hydrocarbon partial pressures, a
23 situation that was quantified formally by calculating the corresponding reaction orders.

1 Aimed at characterizing the kinetic performance of the Mo-V-Te-Nb catalyst in the ODH
2 of ethane, two kinetic models were proposed and the corresponding parameters obtained via a
3 nonlinear regression of the available experiments. Kinetic modeling results are consistent for the
4 two mechanisms proposed indicating that the oxydehydrogenation of ethane to yield ethylene is
5 the reaction with the lowest activation energy, while the re-oxidation of ethylene to CO_x are the
6 most energetically demanding steps, particularly, the its deep oxidation to CO₂. Concerning the
7 adsorption parameters, products re-adsorption competes with reagent(s) adsorption for the active
8 sites of the catalyst. The two sites LH mechanism exhibited a better capacity to represent the
9 experimental information compared with the ER. The adsorption parameters estimated for both
10 kinetic models suggest that competitive adsorption between reagents and products exists in the
11 two mechanisms at relatively high severity reaction conditions, and that CO_x re-adsorption is
12 stronger in comparison with that of water.

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14 **5. References**

- 15 1. Lippe D. Ethylene Markets Return to Normal. *Oil Gas J.* 2011; 109 (10); 94-99.
- 16 2. Lyondellbasell. Ethylene, product stewardship guidance manual. American Chemistry
17 Council. December 2004
- 18 3. Bhasin MM. Is True Ethane Oxydehydrogenation Feasible?. *Top. Catal.* 2003; 23(1-2);
19 145-149.
- 20 4. Cavani F, Ballarini N, Cercola A. Oxidative Dehydrogenation of Ethane and Propane: How
21 Far from Commercial Implementation?–*Cat. Today* 2007; 127; 113-131.
- 22 5. Weissermel K, Arpe H. *Industrial Organic Chemistry*, 3rd ed. Weinheim. Wiley-VCH,
23 1997.
- 24 6. Van Goethem MWM, Barendregt S, Grievink J, Moulijn JA, Verheijen PJT. Ideal
25 Chemical Conversion Concept for the Industrial Production of Ethene from Hydrocarbons.
26 *Ind. Eng. Chem. Res.* 2007; 46 (12); 4045-4062.

- 1 7. Ferrer Soto, Julio Cesar. Suministro de etano PEMEX gas y petroquímica básica al
2 proyecto ETILENO XXI. PGPB 2011, Villahermosa, Tabasco.
- 3 8. Thorsteinson EM, Young FG. US Patent 4,250,346; 1981, assigned to Union Carbide
- 4 9. Bhasin MM, McCain JH, Vora BV, Imai T, Pujadó PR. Dehydrogenation and
5 Oxydehydrogenation of Paraffins to Olefins. *Appl. Catal. A* 2001; 221; 397-419
- 6 10. Thorsteinson EM, Wilson TP, Young FG, Kasai PH. The oxidative Dehydrogenation of
7 Ethane over Catalyst Containing Mixed Oxides of Molybdenum and Vanadium. *J. Catal.*
8 1978; 52(1); 116-132
- 9 11. Cavani, F.; Trifirò, F. The Oxidative Dehydrogenation of Ethane and Propane as an
10 Alternative Way for the Production of Light Olefins. *Cat. Today* 1995; 24; 307-313
- 11 12. Arnold SC, Gaffney AM, Song R, Yuan Yeh C.; US Patent 0,256,432A1; 2010; assigned to
12 Lummus, Novolent GmbH/Lummus Technology Inc..
- 13 13. Botella P, García-González E, Dejoz A, Lopez Nieto JM, Vázquez MI, González-Calbet J.
14 Selective Oxidative Dehydrogenation of Ethane on MoVTeNbO Mixed Metal Oxide
15 Catalyst. *J. Catal.* 2004; 225 (2); 428-438.
- 16 14. Xie Q, Chen L, Weng W, Wan H. Preparation of MoVTe(Sb)Nb Mixed Oxide Catalyst
17 Using a Slurry Method for Selective Dehydrogenation of Ethane. *J. Mol. Catal. A: Chem*
18 2005, 240, 191-196.
- 19 15. Valente JS, Quintana-Solórzano R, Armendáriz-Herrera H, Barragán-Rodríguez G, López-
20 Nieto JM. Kinetic Study of Oxidative Dehydrogenation of Ethane over MoVTeNb Mixed-
21 Oxide Catalyst. *Ind. Eng.Chem.Res.* [dx.doi.org/10.1021/ie402447h](https://doi.org/10.1021/ie402447h)
- 22 16. Hans-Günther L, Andreas R. Alternative Reaction Engineering Concepts in Partial
23 Oxidations on Oxidic Catalysts. *Cat. Rev.-Sci. Eng.* 2007; 49; 1-32.
- 24 17. Klose F, Joshi M, Hamel C, Seidel-Morgenstern A. Selective Oxidation of Ethane over a
25 VO_x/γ-Al₂O₃ Catalyst – Investigation of the Reaction Network. *Appl. Catal. A* 2004; 26;
26 101-110.
- 27 18. Lemonidou AA, Heracleous E. Ni-Nb-O Mixed Oxides as Highly Active and Selective
28 Catalyst for Ethane Production via Ethane Oxidative Dehydrogenation. Part II: Mechanistic
29 Aspects and Kinetic Modeling. *J. Catal.* 2006; 237; 175-189.

- 1 19. Gaab S, Find J, Müller TE, Lercher JA. Kinetics and Mechanism of the Oxidative
2 Dehydrogenation of Ethane over Li/Dy/Mg/O/(Cl) Mixed Oxide Catalysts. *Top. Catal.*
3 2007; 46 (1-2); 101-110.
- 4 20. Kaddouri A, Anouchinsky R, Mazzocchia C, Madeira LM, Portela MF. Oxidative
5 Dehydrogenation of Ethane on the α and β phases of NiMoO₄. *Cat. Today* 1998; 40 (2-3);
6 201-206.
- 7 21. Malleswara-Rao TV, Deo G. Steady State Kinetic Parameters of Bulk V₂O₅ for Ethane and
8 Propane Oxidation Reactions. *Catal. Commun.* 2007; 8; 957-962.
- 9 22. Iglesia E, Argyle M D, Chen K, Bell AT. Ethane Oxidative Dehydrogenation Pathways on
10 Vanadium Oxide Catalysts. *J. Phys. Chem. B* 2002; 106; 5421-5427.
- 11 23. Grabowski R, Sloczynski J. Kinetics of Oxidative Dehydrogenation of Propane and Ethane
12 on VO_x/SiO₂ Pure and with Potassium Additive. *Chem. Eng. Process.* 2006; 44; 1082-1093.
- 13 24. Mears DE. Test for Transport Limitations in Experimental Catalytic Reactors. *Ind. Eng.*
14 *Chem. Process. Des. Dev.* 1997; 10; 541-547.
- 15 25. Pérez-Ramírez J, Berger RJ, Mul G, Kapteijin F, Moulijn JA. The Six Flow Reactor
16 Technology: A Review of Fast Catalyst Screening and Kinetic Studies. *Catal. Today* 2000;
17 60(1-2); 93-109.
- 18 26. López-Nieto JM, Solsona B, Ivars F, Concepción P, Melo F. *Adv. in Chem. Eng.*, 2010,
19 149 - 174.
- 20 27. Petzold LR, Hindmarsh C. LSODA Solver for Ordinary Differential Equations, Livermore
21 National Laboratory, Livermore, CA, U.S.A. 1997.
- 22 28. Boggs PT, Byrd RH, Rogers JE, Schnabel RB. ODRPACK V. 2.01 Software for Weighted
23 Orthogonal Distance Regression, National Institute of Standards and Technology.
24 Gaithersburg, MD, U.S.A. 1992.
- 25 29. Heynderickx MP, Thybaut JW, Poelman H, Poelman D, Marin GB. Kinetic Modeling of
26 the Total Oxidation of Propane over CuO-CeO₂/ γ -Al₂O₃. *App. Catal. B* 2010; 95; 26-38.
- 27 30. Thybaut JW, Saeys M, Marin GB. Hydrogenation Kinetics of Toluene on Pt/ZSM-22.
28 *Chem. Eng. J.* 2002; 90; 117-129.
- 29 31. Dumesic JA, Rudd DF, Aparicio LM, Rekoske JE, Treviño AA, The microkinetics of
30 heterogeneous catalysis. ACS Professional Reference Book, American Chemical Society,
31 Washington, DC, 1993.

- 1 32. Boudart M, Mears DE, Vannice MA. Kinetics of Heterogeneous Catalytic Reactions, Ind.
 2 Chim. Belg. 1967; 32; 281-284
- 3 33. Hercigonja R., Rac V., Rakic V., Auroux A. J. Chem. Thermod., 2012, 48, 112–117.
- 4 34. Brundege J, Parravano G. The Distribution of Reaction Rates and Activation Energies on
 5 Catalytic Surfaces: Exchange Reaction between Gaseous Benzene and Benzene Adsorbed
 6 on Platinum. J. Catal. 1963; 2; 380-396

7

8 **Nomenclature**

9 Roman symbols:

10	A_i	pre-exponential factor of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h kPa})^{-1}$ or $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
11	$A_{\text{rep},i}$	reparameterized pre-exponential factor of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h kPa})^{-1}$ or
12		$\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
13	C_2	ethane
14	CO_x	$\text{CO}_2 + \text{CO}$
15	E_i	activation energy of reaction, $\text{kJ}(\text{mol})^{-1}$
16	F_i^0	reactor inlet molar flow rate of species i , $\text{mol}(\text{h})^{-1}$
17	F_i	reactor outlet molar flow rate of species i , $\text{mol}(\text{h})^{-1}$
18	j	species, experiment or reaction
19	i	species, experiment or reaction
20	k	number of factors in the experimental design
21	k_i	rate coefficient of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h kPa})^{-1}$ or $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
22	M_i	molecular mass of species i
23	n_{resp}	number of responses per experiment
24	n_{obs}	number of independent experiments
25	N_2	nitrogen

1	n_r	number of reactions
2	n_{spec}	number of species
3	O_2	oxygen
4	P_i^0	inlet partial pressure of species i , kPa
5	P_i	partial pressure of species i , kPa
6	R_i	net rate of production (or overall rate) of species i , $\text{mol (g}_{\text{cat}} \text{ h)}^{-1}$
7	r_i	rate of reaction i , $\text{mol (g}_{\text{cat}} \text{ h)}^{-1}$
8	RSS	residual sum of squares
9	S	active site
10	T	temperature, K
11	t	time, min or h
12	T_m	average temperature, K
13	W/F_i^0	Space-time, $\text{g}_{\text{cat}} \text{ h}(\text{mol}_{\text{hydrocarbon}})^{-1}$
14	w_j	weight factor in the objective function
15	W	mass of catalyst, g
16	$\hat{Y}_{i,j}$	predicted yields, $\text{mol}_{\text{species } i} (\text{mol}_{\text{ethane}})^{-1}$
17	Y_{ij}	experimental molar yields designated, $\text{mol}_{\text{species } i} (\text{mol}_{\text{ethane}})^{-1}$
18		
19	Greek symbols	
20	α_i ,	reaction order associated with the partial pressure of ethane for reaction i
21	β_i ,	reaction order associated with the partial pressure of ethane for reaction
22	β	vector of parameters in the objective function
23	ΔH_j^0	standard enthalpy of adsorption of species j , kJ (mol)^{-1}

- 1 $\Delta S_{\text{rep},j}^{\circ}$ reparameterized standard entropy of adsorption of species j, kPa
- 2 ΔS_j° standard enthalpy of adsorption of species j, J (mol K)⁻¹
- 3 θ_j fractional site coverage of a species j.
- 4 θ_s fraction of free active sites.
- 5 $\nu_{j, i}$ stoichiometric coefficients of species j in reaction i

6

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Table 1. Set of elementary steps accounted for in the LH mechanism to describe the ODH of ethane. The two types of free surface sites composing the catalyst are denoted as S_1 and S_2 .

Step ID	Elementary reaction
a	$C_2H_6 + S_1 \xrightleftharpoons{K_{C_2H_6}} C_2H_6-S_1$
b	$O_2 + 2S_2 \xrightleftharpoons{K_{O_2}} 2O-S_2$
1	$C_2H_6-S_1 + O-S_2 \xrightarrow{k_1} \dots \rightarrow C_2H_4-S_1 + H_2O-S_2$
2	$C_2H_6-S_1 + O-S_2 \xrightarrow{k_2} \dots \xrightarrow{6O-S_2} 2CO_2-S_2 + 3H_2O-S_2 + 2S_2 + S_1$
3	$C_2H_6-S_1 + O-S_2 \xrightarrow{k_3} \dots \xrightarrow{4O-S_2} 2CO-S_2 + 3H_2O-S_2 + S_1$
4	$C_2H_4-S_1 + O-S_2 \xrightarrow{k_4} \dots \xrightarrow{5O-S_2} 2CO_2-S_2 + 2H_2O-S_2 + 2S_2 + S_1$
5	$C_2H_4-S_1 + O-S_2 \xrightarrow{k_5} \dots \xrightarrow{3O-S_2} 2CO-S_2 + 2H_2O-S_2 + S_1$
c	$C_2H_4-S_1 \xrightleftharpoons{K_{C_2H_4}} C_2H_4 + S_1$
d	$CO_2-S_2 \xrightleftharpoons{K_{CO_2}} CO_2 + S_2$
e	$CO-S_2 \xrightleftharpoons{K_{CO}} CO + S_2$
f	$H_2O-S_2 \xrightleftharpoons{K_{H_2O}} H_2O + S_2$

Table 2. Series of elementary steps accounted for to propose the ER mechanism to describe the ODH of ethane. S represents a free surface active site.

Step ID	Elementary reaction
a	$O_2 + 2-S \xrightleftharpoons{K_{O_2}} 2O-S$
1	$C_2H_6 + O-S \xrightarrow{k_1} \dots \rightarrow C_2H_4 + H_2O-S$
2	$C_2H_6 + O-S \xrightarrow{k_2} \dots \xrightarrow{60-S_2} 2CO_2-S + 3H_2O-S + 4-S$
3	$C_2H_6 + O-S \xrightarrow{k_3} \dots \xrightarrow{40-S_2} 2CO + 3H_2O-S + 2-S$
4	$C_2H_4 + O-S \xrightarrow{k_4} \dots \xrightarrow{50-S_2} 2CO_2 + 2H_2O-S + 4-S$
5	$C_2H_4 + O-S \xrightarrow{k_5} \dots \xrightarrow{30-S_2} 2CO + 2H_2O-S + 2-S$
b	$CO_2-S \xrightleftharpoons{K_{CO_2}} CO_2 + S$
c	$CO-S \xrightleftharpoons{K_{CO}} CO + S$
D	$H_2O-S \xrightleftharpoons{K_{H_2O}} H_2O + S$

Table 3. LH kinetic model parameters including activation energies, reparameterized pre-exponential factors, adsorption enthalpies and reparameterized adsorption entropies. Confidence intervals at the 95 % probability are also displayed for the parameters estimated via a nonisothermal regression.

Reaction	E, kJ(mol) ⁻¹	A _{rep} , mol(g _{cat} ·h) ⁻¹	A, mol(g _{cat} ·h) ⁻¹
C ₂ H ₆ +0.5O ₂ →C ₂ H ₄ +H ₂ O	114.9 ± 5.8	6.7×10 ⁻² ± 2.1 ×10 ⁻³	1.8×10 ⁷
C ₂ H ₆ +3.5O ₂ →2CO ₂ +3H ₂ O	122.7 ± 16.6	9.9×10 ⁻⁴ ± 6.9 ×10 ⁻⁵	9.6×10 ⁵
C ₂ H ₆ +2.5O ₂ →2CO+3H ₂ O	156.5 ± 30.2	3.9×10 ⁻⁸ ± 4.6 ×10 ⁻⁹	1.1×10 ⁴
C ₂ H ₄ +2O ₂ →2CO ₂ +2H ₂ O	190.0 ± 22.2	6.8×10 ⁻⁴ ± 4.7×10 ⁻⁵	5.6×10 ¹⁰
C ₂ H ₄ +2O ₂ →2CO+2H ₂ O	177.8 ± 15.4	2.1×10 ⁻³ ± 1.2×10 ⁻⁴	2.2×10 ¹⁰

Species	ΔH ⁰ , kJ(mol) ⁻¹	ΔS _{rep} ⁰ , (kPa) ⁻¹	ΔS ⁰ , J(mol K) ⁻¹
Ethane	-21.5 ± 5.9	1.1×10 ⁻¹ ± 5.9 ×10 ⁻³	-48.6
Ethylene	-64.0 ± 9.0	5.2×10 ⁻¹ ± 3.6×10 ⁻²	-95.2
Oxygen	-62.7 ± 15.0	1.6×10 ⁰ ± 2.2 ×10 ⁻¹	-84.3
CO ₂	-80.3 ± 20.0	5.1×10 ⁻² ± 6.8×10 ⁻³	-137.4
CO	-80.0 ± 27.8	6.0×10 ⁻¹ ± 2.2×10 ⁻²	-116.7
H ₂ O	-20.7 ± 4.6	3.8×10 ⁻³ ± 3.8×10 ⁻⁴	-75.2

F_{reg}= 1981, F_{tab}= 2.79, t_{tab}=1.97 at 1-α = 0.95 and 404 degrees of freedom

Table 4. ER kinetic model parameters including activation energies, reparameterized pre-exponential factors, adsorption enthalpies and reparameterized adsorption entropies.

Confidence intervals at the 95 % probability are also presented for the parameters estimated via a nonisothermal regression.

Reaction	E, kJ(mol) ⁻¹	A _{rep} , mol(g _{cat} h kPa) ⁻¹	A, mol(g _{cat} h kPa) ⁻¹
C ₂ H ₆ +0.5O ₂ →C ₂ H ₄ +H ₂ O	108.2 ± 8.8	2.4×10 ⁻³ ± 8.9×10 ⁻⁵	2.0×10 ⁵
C ₂ H ₆ +3.5O ₂ →2CO ₂ +3H ₂ O	124.6 ± 8.9	5.3×10 ⁻⁵ ± 3.7×10 ⁻⁶	7.1×10 ⁴
C ₂ H ₆ +2.5O ₂ →2CO+3H ₂ O	193.4 ± 42.3	1.4×10 ⁻⁷ ± 2.0×10 ⁻⁸	2.0×10 ⁷
C ₂ H ₄ +2O ₂ →2CO ₂ +2H ₂ O	187.7 ± 28.4	5.5×10 ⁻⁵ ± 4.1×10 ⁻⁶	3.1×10 ⁹
C ₂ H ₄ +2O ₂ →2CO+2H ₂ O	181.2 ± 12.9	2.0×10 ⁻⁴ ± 9.8×10 ⁻⁶	3.8×10 ⁹

Species	ΔH ⁰ , kJ(mol) ⁻¹	ΔS _{rep} ⁰ , (kPa) ⁻¹	ΔS ⁰ , J(mol K) ⁻¹
Oxygen	-38.1 ± 7.4	4.0×10 ⁰ ± 4.4×10 ⁻¹	-42.0
CO ₂	-102.5 ± 30.7	1.6×10 ⁰ ± 2.1×10 ⁻¹	-139.9
CO	-137.5 ± 46.7	5.9×10 ⁻¹ ± 7.0×10 ⁻²	-197.1
H ₂ O	-43.0 ± 13.0	9.2×10 ⁻⁴ ± 7.4×10 ⁻⁵	-118.4

F_{reg}= 1078, F_{tab}= 2.79, t_{tab}=1.97 at 1-α = 0.95 and 408 degrees of freedom