



Understanding the kinetic behavior of a Mo–V–Te–Nb mixed oxide in the oxydehydrogenation of ethane



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HIGHLIGHTS

- The oxydehydrogenation of ethane to ethylene was studied over a MoVNbTe catalyst.
- Experiments and kinetics were combined to understand the catalyst's behavior.
- Langmuir–Hinshelwood and Eley–Rideal kinetics were developed.
- Models parameters were thermodynamically and statistically consistent.
- Modeling results indicated that products re-adsorption may be important.

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ABSTRACT

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

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1. Introduction

Ethylene is, undoubtedly, the primary product in the petrochemical industry [1]. Even though the number of direct end-uses of ethylene is certainly limited, it is the base raw material for manufacturing polymers, e.g., polyethylene, polystyrene and polyethyl-

ene chloride, together with other important chemical compounds standing out ethylene oxide, ethanol and polyvinyl acetate [2]. Worldwide, ethylene is mostly produced from the steam cracking of hydrocarbons [3] and, to a lesser extent, via direct dehydrogenation of ethane in the presence or in the absence of catalyst [4]. A common characteristic of these two processes is that they are performed at high temperature (1025 K+) due to thermodynamic matters [5]. Evidently, high temperature operation increases the installation costs as well as the operation expenses and, additionally, leads to a large diversity of byproducts, a low ethylene yield and coke formation [6].

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Nomenclature

Roman symbols

A_i	pre-exponential factor of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h kPa})^{-1}$ or $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
$A_{\text{rep},i}$	reparameterized pre-exponential factor of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h kPa})^{-1}$ or $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
COx	$\text{CO}_2 + \text{CO}$
E_i	activation energy of reaction i , $\text{kJ}(\text{mol})^{-1}$
F_i^o	reactor inlet molar flow rate of species i , $\text{mol}(\text{h})^{-1}$
F_i	reactor outlet molar flow rate of species i , $\text{mol}(\text{h})^{-1}$
j	species, experiment or reaction
i	species, experiment or reaction
k_i	rate coefficient of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h kPa})^{-1}$ or $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
M_i	molecular mass of species i
n_{resp}	number of responses per experiment
n_{obs}	number of independent experiments
N_2	nitrogen
n_r	number of reactions
n_{spec}	number of species
O_2	oxygen
P_i^o	inlet partial pressure of species i , kPa
P_i	partial pressure of species i , kPa
R_i	net rate of production (or overall rate) of species i , $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$
r_i	rate of reaction i , $\text{mol}(\text{g}_{\text{cat}} \text{ h})^{-1}$

RSS	residual sum of squares
S	active site
T	temperature, K
t	time, min or h
T_m	average temperature, K
W/F_i^o	space-time of experiment i , $\text{g}_{\text{cat}} \text{ h}(\text{mol}_{\text{hydrocarbon}})^{-1}$
w_j	weight factor of response j in the objective function
W	mass of catalyst, g
\hat{Y}_{ij}	predicted molar yields, $\text{mol}_{\text{species}i}(\text{mol}_{\text{ethane}})^{-1}$
Y_{ij}	experimental molar yields, $\text{mol}_{\text{species}i}(\text{mol}_{\text{ethane}})^{-1}$

Greek symbols

α_i	reaction order associated with the partial pressure of ethane for reaction i
β_i	reaction order associated with the partial pressure of oxygen for reaction i
β	vector of parameters in the objective function
ΔH_j^o	standard enthalpy of adsorption of species j , $\text{kJ}(\text{mol})^{-1}$
$\Delta S_{\text{rep},j}^o$	reparameterized standard entropy of adsorption of species j , kPa
ΔS_j^o	standard enthalpy of adsorption of species j , $\text{J}(\text{mol K})^{-1}$
θ_j	fractional site coverage of species j
θ_s	fraction of free active sites
$\nu_{j,i}$	stoichiometric coefficients of species j in reaction i

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

Aimed at diversifying the options for producing ethylene and, at the same time, overcoming the inconveniences of the existing commercial processes outlined above, attention has been paid on alternative processes [8]. Among them, the catalytic oxidative dehydrogenation (ODH) of ethane is, undeniably, one of the most promising options. The ODH of ethane is an exothermic process that involves the reaction between ethane and an oxidant, usually oxygen [9]. Such a partial oxidation process is, however, inevitably accompanied by the formation of CO and CO_2 referred to as COx, which are produced via very exothermic reactions. Apart from exhibiting a good capacity to activate the corresponding alkane at relatively low temperatures, catalytic systems to be applied to the ODH of ethane must display a remarkably high selectivity for ethylene; in other words, reducing the COx production to a minimum level. Even though the list of catalysts proposed for the ODH of ethane is extensive [10–14], multimetallic mixed oxides containing Mo, Te, V and Nb have been reported as one of the most promising catalytic systems in view of their high activity to convert ethane and selectivity to produce ethylene [12,14]. For instance, a bimetallic Ni–W–O mixed metal oxide catalyst exhibited selectivities to ethylene as high as 80% at relatively low temperatures (<673 K) accompanied, however, by relatively low values of ethane conversion. Increasing the reaction temperature

leads to higher ethane conversions but the ethylene selectivity decreases notoriously [13].

The Mo–V–Te–Nb system is essentially composed of two crystalline phases designated M1 and M2. M2 is a hexagonal phase, which is practically inactive for the ODH of ethane as does not contain sites to activate this alkane [14,15]. M1 is an orthorhombic phase that contains the active/selective sites to activate ethane in partial oxidation reactions [16–19]. Generally, the (001) plane of M1 crystalline phase has been reported as the plane containing the active sites for ODH of ethane. In a recent publication [20], authors found a good correlation between the catalytic performance and the crystallinity properties of the M1 phase. Notwithstanding, they stated that the lateral termination of the rod shaped M1 particles can provide potential active ensembles, which would improve to the overall catalyst's performance. Hence, considering that two types of active sites are involved in the ODH of ethane process appears to be a reasonable approach.

Some previous publications [14a,b,15] indicate that the Mo–V–Te–Nb system starts to be active for the ODH of ethane below 573 K, a temperature substantially lower than the one required by the existing commercial technologies. Besides leading to a significant energy saving, lowering the operation temperature reduces the incidence of side reactions and, hence, the number of byproducts. An additional important challenge associated with the ODH of ethane concerns with the reactor configuration due to the amount of heat released by the various chemical processes involved. Evidently, having reliable kinetic models at hands is a basic requirement for performing reactor design, scale-up and optimization [21]. Kinetic models for describing the ODH of ethane, which have been constructed on the basis of Power Laws (PL) empiricism as well as Langmuir–Hinshelwood, Eley–Rideal, and Mars–van Krevelen mechanisms [22–29] are already available in the literature. Nonetheless, such models are, strictly speaking, valid for the corresponding catalyst composition.

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