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# Niobium as promoting agent for selective oxidation reactions

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ABSTRACT

Literature reports a significant number of studies that describe the various niobium-based catalysts for many uses; selective oxidation reactions constitute a significant part of those works. This contribution makes a brief revision of literature that investigates the promoting effect of niobium on different catalytic formulations used for selective oxidation reactions rather than in the use of niobium as main component.

## 1. Introduction

Niobium (named after Niobe, the daughter of Tantalus, according to Greek Mythology) was discovered in 1801 by Charles Hatchett while he was working for the British Museum and analyzed a piece of columbite. Columbite turned out to be a very complex mineral, and he discovered that it contained a ‘‘new earth’’ which implied the existence of a new element. Hatchett was able to isolate the oxide of the new element and establish its chemical identity; thus, he named the element columbium and the mineral columbite in honor of the Spanish sailor Christopher Columbus, since this mineral was found in America. In the following year, 1802, Anders G. Ekeberg claimed to have identified a new element while he was studying some Finnish minerals, he called the new element tantalum (it refers to Tantalus, the mythical son of the god Zeus). It was thought that the two elements, columbus and tantalum were the same until 1844, when Heinrich Rose, examining a sample of columbite, reported that two distinct elements were present in such sample. He reported one as Ekeberg's tantalum and he called the other as niobium (after Niobe, the daughter of Tantalus). Despite the chronological precedence of Hatchett's finding, the name niobium was adopted by the IUPAC (International Union for Pure and Applied Chemistry) in 1950 after 100 years of controversy [1].

Niobium is an important element in catalysis and its properties have been extensively analysed [2,3]. It is an active component of many catalytic systems and it has been used in the formulations of catalysts during the last two decades since many catalytic applications of niobium materials were discovered during the 1970s and 80s. Nowadays, a continuous effort is being made in the catalytic research with niobium materials in the form of compounds/complexes, mixed bulk oxides, oxide supports and surface niobium oxide phases.

Niobium-based materials are effective catalysts for many catalytic reactions; literature reports a significant number of patents and papers describing various uses of niobium-based catalysts. Ziolek and Nowak reviewed the structures, characterization and applications of niobium compounds [4]. Nb-based materials find many catalytic applications, for example, niobium oxide ($Nb_2O_5$) is a highly effective oxide support material for metallic catalysts [5]. There are a significant number of niobium-containing materials (i.e. $NbCl_5$, $NbF_5$, NbH, $NbS_2$, NbN, NbC, $NbO_x$ and Nb organometallic compounds) that find catalytic applications [2]. Other compounds, as niobic acid, catalyze some reactions, since it is used in hydration, estherification and condensation processes.

Niobium is not only a major component in many catalysts; in addition, there is an increasingly important number of applications in which niobium is a key promoter. Niobium has a rich complex chemistry, and it reacts with many elements of the periodic table to form a wide range of compounds and oxide phases with complex structures [6]. The use of niobium as a promoter is of paramount importance and it has not been addressed properly so far. This review highlights the catalytic applications of niobium as a promoting agent for selective oxidation reactions (Scheme 1). The uses of niobium as main component in the formulation of catalysts will not be considered.

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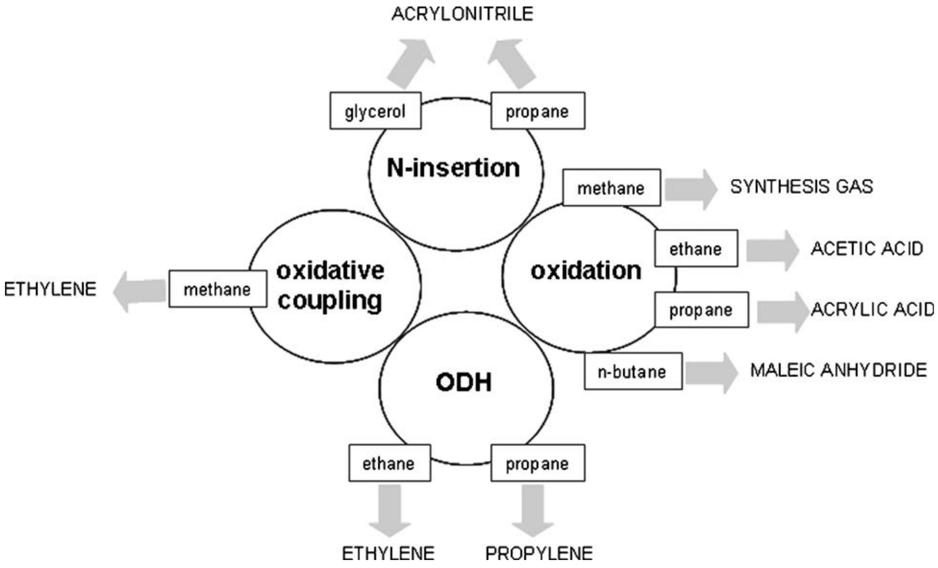


**Scheme 1.** Selective oxidation reactions in which N is used as promoting agent of the catalysts.

## 2. Principal catalytic applications of Nb as a promoting agent during oxidation reactions

### 2.1. Oxidative dehydrogenation lower alkanes

Oxidative dehydrogenation involves the partial oxidation of a lower alkane in the presence of oxygen to yield the corresponding alkene, according to reaction (1).

$$C_nH_{2n+2} + O_2 \rightarrow C_nH_{2n} + H_2O \qquad (1)$$

Early studies by Burch and Swarnakar [7] and Thorsteinson et al. [8] reported an enhancement in activity in the dehydrogenation of ethane when niobium is added to the Mo-V-O catalysts. BASF filed several patents in which the promoting effect of Nb has a remarkable effect on Mo-V-O based catalysts for the dehydrogenation of propane [9,10]. By 2003, Tanabe [2] reviewed the promoting effect of Nb to the Mo-V oxide catalytic system for the ethane oxidative dehydrogenation (ODH) to ethylene. It is shown how catalytic systems containing Nb are more active and selective. The role of niobium is to enhance the intrinsic activity of Mo–V oxide system improving the selectivity by inhibiting the total oxidation of ethane to carbon dioxide avoiding the formation of segregated $MoO_3$ and/or $V_2O_5$ crystalline phases.

Nb may affect the selectivity of vanadium oxide catalysts to propylene during the oxidative propane dehydrogenation through modifications on its Lewis acidity [11,12]; niobium promotes the presence of vanadium sites exhibiting acidic and redox properties [13] different to those of bulk vanadium oxide. Grzybowska et al. studied the effect of adding Nb to vanadium oxide supported on $SiO_2$ and MgO catalysts [14,15]. They avoided the formation of mixed Nb–V bulk oxide compounds and observed an increase in the specific activity during propane ODH reaction. They correlate this enhancement in the catalytic properties with an increase in the number of acid sites of both Lewis and Brønsted types; such a promoting effect would not be observed if mixed Nb–V oxide phases form. Accordingly, Cavani and co-workers have studied the effect of doping vanadium catalysts with niobium for the oxidative dehydrogenation of propane to propylene [16]. They detected mixed V–Nb–O structures, as $VNbO_4$ and $VNbO_5$, at high niobium contents, which are detrimental for the oxidative dehydrogenation of propane, since they produce propylene with a very low selectivity and the main products are carbon oxides. Such mixed oxides are not capable to furnish oxygen for the abstraction of hydrogen from propane, and only act as dehydrogenating catalysts when propane is the only reactant. Predieri and co-workers [17] also studied different materials containing the $VNbO_5$ phase and found higher propylene selectivities for catalysts with lower niobium loading; in addition, they found that a mechanical mixture of $V_2O_5$ and $Nb_2O_5$, in which mixed V–Nb–O compounds were not detected, yielded more propylene than the catalysts containing such mixed phases. Wendt et al. reported that doping of $V_2O_5$-$ZrO_2$ catalysts with niobia caused a decrease in the catalytic activity during the ODH of propane due to the formation of V–O–Nb species [18]. Busca et al. [19] studied Nb as additive of vanadium-silica catalysts and found that V–Nb–O mixed phases were formed. They reported that Nb did not enhance the catalytic performance of the V-Si catalysts. So, it seems that Nb enhances the catalytic properties of vanadium catalysts for propane oxidehydrogenation only when it does not form mixed V–Nb–O phases. This improvement of the propylene selectivity is attributed to the acidic properties of niobium, which increase the number of acid sites of the catalysts. The MgO-supported vanadium oxide catalysts do not appear to behave as other bulk or supported vanadium oxide catalysts. The selectivity to propene does not depend clearly on the acid–basic properties and it does not improve upon niobium addition.

Selectivity to ethane in ethane ODH does not depend on acidic properties [20,21], this accounts for the negligible effect of niobium doping on ethane ODH to ethylene on vanadium oxide based catalysts. However, Nb has been used as an additive to nickel oxide based catalysts for alkane dehydrogenation [22,23]. Recently, Lemonidou and Heracleous have studied the effect of adding niobium to NiO bulk catalysts for the oxidative dehydrogenation of ethane to ethylene [24,25]. They found that small amounts of niobium transform NiO, a total oxidation catalyst, into a catalyst selective for oxidative dehydrogenation of ethane. They proposed that nickel centers constitute the reactive sites for the activation of alkane, whereas niobium would essentially tune selectivity profiles modifying the reaction route from total oxidation to selective ODH. $^{18}O_2$ exchange measurements underline a different distribution of isotopic oxygen species from the niobium doped material with respect to the undoped NiO catalyst. The prevalent formation of cross-labelled oxygen species on NiO indicates that there is a fast oxygen dissociation step in the exchange process, leading to large concentration of intermediate electrophylic surface oxygen species, active for total oxidation of ethane. Larger amounts of isotopic doubly exchanged species were observed on the Ni-Nb-O catalyst; thus, niobium enhances the surface diffusion step, suppressing the formation of highly oxidizing species. Again, effective ODH catalysts require small amounts of niobium; $Nb^{5+}$ ions would efficiently substitute $Ni^{2+}$ ions filling the cationic vacancies in the NiO lattice. A high Nb content leads to saturation of the bulk lattices sites and formation of the mixed $NiNb_2O_6$ phase and pure $Nb_2O_5$, and the selectivity to ethylene decreases. Promoting effect of niobium is bound to an incipient interaction with nickel or vanadium oxide phases.

### *2.2. Oxidation of ethane to acetic acid*

Propane can be partially oxidized in the presence of molecular oxygen to obtain acetic acid according to reaction (2).

$$CH_3{-}CH_3 + 3/2O_2 \rightarrow CH_3{-}COOH + H_2O \qquad (2)$$

Nb is used as an additive of Mo-Pd-O based catalysts for the selective production of acetic acid from ethane and/or ethylene [26]. The promoting effect of doping Mo-V-O based catalysts with Nb for the selective oxidation of ethane to acetic acid was investigated by López Nieto and co-workers [27]. They detected the presence of $MoO_2$ crystalline phase in the samples prepared in the absence of Nb. $MoO_2$ is unselective for the formation of acetic acid. XRD patterns showed that the incorporation of small amounts of niobium increases reflections corresponding to $Mo_6V_9O_{40}$ and $Mo_4V_6O_{25}$ phases whereas the presence of mixed phases containing Nb is not conclusive. The results showed that the catalytic activity is related to the presence of vanadium centers and that niobium incorporation improves the catalytic activity.

In a recent study [28], the influence of niobium additive to the Mo-V-O catalytic system for this reaction was reported by Bordes-Richard et al. The results are in the same line than those obtained by López Nieto's group. The niobium containing catalysts are almost amorphous materials that are made up of nanocrystalline particles of vanadium, as niobium-doped Mo–V–O mixed phases and are active and very selective to ethylene and acetic acid. The presence of small amounts of niobium modifies vanadium centers triggering the formation of mixed Mo–V–O structures, which in turn make the catalyst more active and selective towards acetic acid formation.

### *2.3. Oxidation and ammoxidation of propane*

Propane can be partially oxidized in the presence of molecular oxygen and water to yield acrylic acid of in the presence of ammonia and oxygen to yield acrylonitrile according to reactions (3) and (4), respectively.

$$CH_3{-}CH_2{-}CH_3 + 2O_2 \rightarrow CH_2{=}\,CH{-}COOH + 2H_2O \qquad (3)$$

$$CH_3{-}CH_2{-}CH_3 + 2O_2 + NH_3 \rightarrow CH_2{=}\,CH{-}CN + 4H_2O \qquad (4)$$

The synthesis of chemicals intermediates, as acrylonitrile and acrylic acid, directly from propane is an important process since both compounds are useful chemicals as raw materials for various synthetic resins, paints, fibers, etc. Nowadays; they are produced from propylene, which is several times more expensive than propane. The replacement of propylene feeds by propane for the production of both acrylonitrile and acrylic acid is an important challenge [29,30]; more recently, the use of renewables as raw materials–glycerol- is becoming a new focus of interest under study (see Glycerol transformation section).

Promising results in both propane oxidation and ammoxidation reaction are obtained with multicomponent Mo-V-Te(Sb)-Nb-O catalysts [31–36]. These mixed-phase catalysts contain the so-called "M1" and "M2" phases with orthorhombic and pseudohexagonal structures, respectively, proposed to be active and selective in propane oxidation to acrylic acid and ammoxidation to acrylonitrile [37–42]. The catalytic performance of such system seems to be strongly influenced by the presence of niobium, even when it is added in small amounts. Early studies indicated that the importance of niobium as additive of this multicomponent catalysts is to produce an optimal distribution between both M1 and M2 phases since the M1 is rich in niobium [43–46] whereas only small amounts of niobium do enter the M2 phase, although it is synthesized in the presence of niobium ions. Thus, synthesis methods able to incorporate niobium in the Mo–V–O framework would render catalysts highly active and selective [47].

Guliants and co-workers studied the Mo-V-O catalytic system doped with niobium for propane (amm)oxidation [48] by methanol and allyl alcohol chemisorption and surface reaction in combination with low energy ion scattering (LEIS) [49]. This study provides evidence for surface depletion for vanadium and molybdenum and enrichments of niobium and tellurium with respect to the bulk composition for the niobium-containing catalyst. The catalyst containing tellurium and niobium was able to oxidize and ammoxidize propane much more actively and selectively than the Mo-V-O catalyst showing that the presence of bulk Te and Nb oxide components in the M1 phase was highly beneficial for the selectivity of the Mo-V-Te-Nb-O catalyst. They propose that niobium has two important roles in the M1 structure: (1) it would provide site isolation of the active centers, which results in highly selective propane (amm) oxidation, and (2) it would stabilize the crystal structure under catalytic reaction conditions. Thus, the Mo-V-O phase is capable of activating propane; however, it shows low catalytic activity and lacks the surface sites that are able to both bind the propylene intermediate strongly and oxidize it further to acrolein and acrylic acid. The addition of the niobium species results in the formation of surface V–O–Nb and Mo–O–Nb bonds enhancing the rates and the selectivity to partial oxidation products. These results underline that the outermost layer may indeed have a major effect on the catalytic performance, and well-defined bulk M1 phase may act as a support that modulates the properties of surface oxide species. Thus, in addition to the site isolation, the surface $NbO_x$ species would moderate the adsorption of reaction intermediates and products preventing over-oxidation of acrylic acid and acrylonitrile. These papers are in line with a previous study by Ueda et al. that concluded that doped niobium occupies the same structural position of V, improving the selectivity to acrylic acid particularly at high conversion region, since the further oxidation of acrylic acid to $CO_x$ is suppressed [50]. In this line, Andersson and co-workers have investigated the effects of substitution of niobium in the M2 phase [51]. They found that pentavalent Nb can substitute both $Mo^{6+}$ and $V^{4+}$ in the M2 structure and this substitution increases the activity during propene ammoxidation. They proposed that the increase of the activity caused by the replacement of small amounts of vanadium by niobium should be due to a secondary effect, considering that Nb-centers usually are not directly involved in the activation of either ammonia or propane. They suggested that tellurium in the hexagonal channels of the M2 structure is displaced from the center of the channel towards vanadium-sites [28]. Thus, replacement of $V^{4+}$ by a larger $Nb^{5+}$ leads to a displacement of tellurium to a position that is apparently more optimal for the activity.

Grasselli and co-workers investigated the role of Nb as additive of the Mo-V-Te-O catalytic system by the replacement of niobium by tantalum [52,53]. They found that the M1-Ta phase in

MoVTaTeO catalysts is isostructural with the M1-Nb phase found in MoVNbTeO catalysts but that a lower amount of $Ta^{5+}$ is required in solution to form the M1 phase. The higher amounts of $Nb^{5+}$ found in M1-Nb results in a higher selectivity toward acrylonitrile. They suggested that an indirect catalytic role of $Nb^{5+}$ in M1-Nb may be to increase the number of acidic $Mo^{6+}$ sites enhancing the acrylonitrile selectivity.

The effect of doping Mo-V-Sb-O and Mo-V-Te-O catalytic systems with niobium was investigated by Ueda and Watanabe [54]. They found that niobium could affect the morphology of catalysts since crystallization is suppressed through the introduction of niobium and prevents the formation of large particles; although niobium is not necessary to construct the orthorhombic structure. They performed reaction network analyses for each catalyst and showed that molybdenum and vanadium in a framework structure are responsible for oxidative activation of propane to propylene, and that tellurium or antimony clearly promotes the conversion of the formed propylene to acrylonitrile, whereas catalysts without tellurium or antimony clearly promote non-selective conversion of propylene to $CO_x$. They proposed that a structural dilution of vanadium in the octahedral network can be achieved as a result of the introduction of niobium in the tellurium-containing system, presumably preventing the further oxidation to $CO_x$; but they do not observed such decrease in the non-selective conversion in the antimony-containing systems; hence, niobium can be substituted by vanadium in the case of the tellurium-containing system but only for molybdenum in the case of the antimony system.

Our group has investigated the effect of niobium addition to Sb-V-O catalysts for the ammoxidation of propane to acrylonitrile [55,56] with niobia-supported Sb-V-O catalysts. We reported that niobium centers are capable of improving the yield to acrylonitrile mainly due to vanadium-niobium oxides interactions [57,58]. The effect of niobium doping strongly depends on the specific preparation method and on the nature of the precursors. Fig. 1 shows the yields versus time on stream obtained for Sb-V-O/Al (A and D) and Sb-V-Nb-O/Al (B, C, E and F) catalysts [55]. The addition of Nb to the formulation of catalysts enhances the acrylonitrile yields in the case of sample with Sb/V = 1 (molar ratio); however, niobium addition has a detrimental effect on the acrylonitrile yields for sample with a Sb/V molar ratio near three. The interplay between vanadium, niobium and antimony is particularly complex; the catalyst becomes little active and selective when the niobium–antimony oxides interaction prevails over the vanadium-antimony or over vanadium niobium interactions Fig. 1A, D, y E; this is consistent with Ueda's work [42] who found that inefficient $SbNbO_4$ phase can be formed at the expense of the efficient $VSbO_4$ phase when the Nb–Sb oxides interaction is favoured by the synthesis method. On the contrary, niobium centers enhanced the catalytic behaviour of such samples when the V–Nb–O interactions are favoured, as shown in Fig. 1B and C. In rutile antimonates, $VSbO_4$, an important role in providing a high selectivity to acrylonitrile in propane ammoxidation is played by the excess of antimony oxide interacting with the $VSbO_4$ rutile surface [59–62]; a similar scenario is observed for Cr/V/Sb mixed oxides, in the absence of niobium [63,64]. Cavani et al. found that Nb addition to rutile type Cr/V/Sb/Nb mixed oxides causes a decrease in activity only in samples with low Sb content whereas the effect on activity is positive in samples (albeit very low) with higher Sb content [65]. Their characterization results excluded the formation of $SbNbO_4$ whereas the formation of $CrNbO_4$ and/or $VNbO_5$ could not be ruled out. They attributed the positive effect of Nb to a modification of the properties of Sb sites at the surface of rutile crystallites, with generation of species with improved catalytic properties in allylic ammoxidation. Niobium species also would increase the concentration of cationic vacancies, which would play an additional role in the selectivity to acrylonitrile. Similar results are also obtained when Nb is added to Sn/V/Sb catalysts since the presence of Nb improves both the activity and the selectivity to acrylonitrile [66]. This effect is attributed to the incorporation of Nb in the rutile-type phase. However, when a large amount of Nb is present in the formulation of catalyst, the presence of $Nb_2O_5$ decreases the selectivity to acrylonitrile.

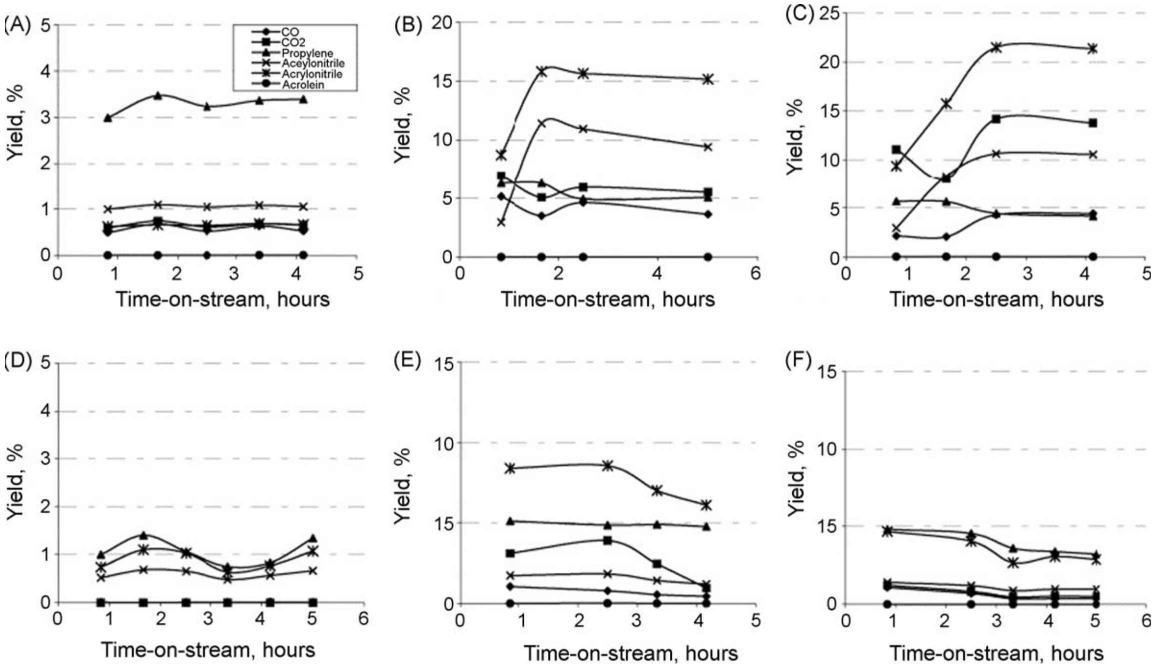


**Fig. 1.** Yields vs. time on stream for (A) 1Sb3V1Nb1/Al-($Sb_2O_3$), (B) 1Sb1V1Nb1/Al-($Sb_2O_3$), (C) 1Sb1V1Nb2/Al-($Sb_2O_3$), (D) 1Sb3V1Nb1/Al-(SbT), (E) 1Sb1V1Nb1/Al-(SbT) and (F)1Sb1V1Nb2/Al-(SbT). Reaction conditions: total flow 20 ml/min; feed composition (vol.%): $C_3H_8/O_2/NH_3/He$ (9.8/25/8.6/56.6), 200 mg of catalysts, temperature 440 °C (reproduced from Ref. [55]).

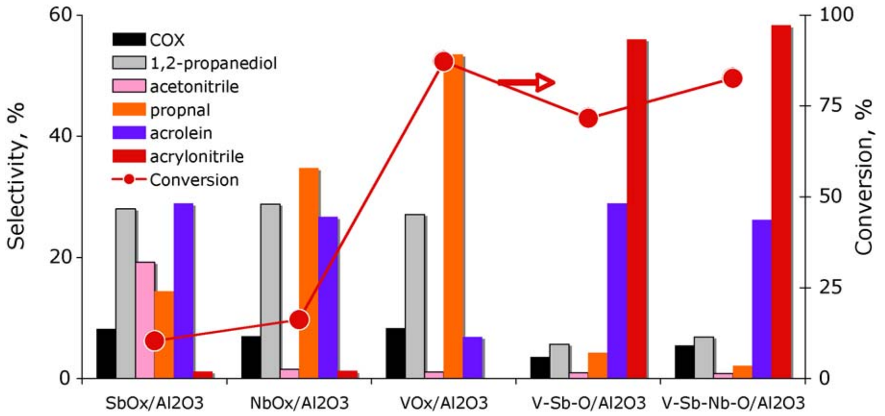


**Fig. 2.** Effect of catalyst composition on the ammoxidation of glycerol. The columns illustrate selectivity and the solid line, glycerol conversion at 400 °C (adapted from Ref. [69]).

### 2.4. Glycerol transformations

Glycerol is an increasingly important molecule in the context of renewable biomass resources since it is a major by-product in the methanolysis during biodiesel production. In this contex, developing selective glycerol-based catalytic processes is a major challenge. $Nb_2O_5$ catalysts are active for the transformation of glycerol to acrolein [67,68]; since acid sites are necessary for such transformation. There are not many processes of glycerol using niobium as a promoter, however, some recent developments underline that it may be a highly convenient additive. A new reaction has been reported, the ammoxidation of glycerol to acrylonitrile [69,70], the presence of niobium is critical to maximize activity and selectivity. The addition of niobium to V-Sb-Al-O catalysts improved the catalytic behaviour of such samples during the catalytic ammoxidation of glycerol (Fig. 2) to acrylonitrile [69,70] since niobium sites increase the acidic properties of the V-Sb-Al-O catalysts. Fig. 2 shows how both glycerol conversion and selectivity to acrylonitrile improved when the alumina-supported Sb-V-O based catalyst is doped with niobium. Alumina supported vanadium oxide, or antimony oxide or niobium oxide are not efficient for converting glycerol to acrylonitrile, but the presence of both, antimony and vanadium oxide o alumina makes the system efficient, glycerol conversion and acrylonitrile selectivity further increase upon niobium doping.

### 2.5. Methane partial oxidation

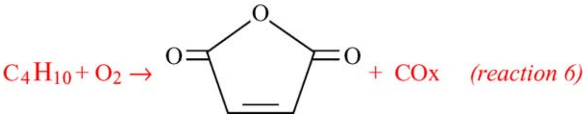
Synthesis gas can be obtained though the methane partial oxidation according to reaction 5 [71]:

$$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO \tag{5}$$

The effect of niobium loading on the catalytic activity of Ce-Zr-Ni-O catalysts during methane partial oxidation has been reported [72]. The catalytic methane partial oxidation (MPO) to synthesis gas is exothermic and yields synthesis gas with an $H_2$/CO ratio of two, which is suitable for methanol and Fischer–Tropsch synthesis. It was demonstrated that niobium species modified the catalytic properties of the Ce-Zr-Ni-O catalysts. The activity decreased and the amount of carbon deposition was increased with increasing amounts of niobium loadings. Niobium addition affects NiO phase, and modifies it reducibility nickel-niobium interaction; in addition, Nb species are responsible of an inhibition of surface oxygen reduction of the Ce–Zr–O mixed phase.

### 2.6. Oxidation of n-butane to maleic anhydride

*n*-Butane can be effectively oxidized to maleic anhydride according to maleic anhydride according to reaction (6).



(6)

The addition of niobium in the form of NbPO to vanadium phosphorus oxide (VPO) catalyst improves its performance for the oxidation of *n*-butane to maleic anhydride [73]. The modified VPO catalyst reaches a stationary state after only 40 h, while the un-doped catalyst alone needs more than 120 h. Electron microscopy underlines how niobium additive promoter local disorder that may act as a promoter for a faster structural rearrangement to the active phase. The addition of Nb also improves the mechanical strength of VPO pellets to be used in fixed bed reactors.

A recent patent filed by Cavani and co-workers [74] claims the effect of niobium as a promoter element for niobium-doped vanadium/phosphorus mixed oxide catalyst when it is added in an amount corresponding to an atomic ratio of vanadium to niobium in the range of 250:1–60:1. Such amount of Nb in the formulation of catalyst improved activity, yield to maleic anhydride and the optimal performance from the very beginning of the catalytic lifetime.

### 2.7. Oxidative coupling of methane

The oxidative coupling of methane to form C2 compounds is an interesting process to produce ethylene in an economic way. Early studies by Ross and co-workers demonstrated that the catalytic activity of Li/MgO catalysts can be significantly improved with the addition of Nb as doping [75,76]. They investigated several additives and the C2 yield (ethane and ethylene) was found highest when Nb is added. Structural investigation showed that the addition of niobium increased the surface area and gave an increase in the lithium content of the calcined catalysts. Two niobium phases, $LiNbO_3$ and $Li_3NbO_4$, were detected and they attributed the high activity to the former.

## 3. Concluding remarks

Niobium rich chemistry makes it an invaluable additive for several oxidation reactions. The promoting effect is mainly due to its ability to combine with many elements forming new compounds. Upon its interaction, it typically modulates redox

**Table 1**
Main applications of Nb as doping agent during partial oxidation reactions with bulk and supported mixed oxides catalysts.

| Catalytic system | Advantages of using Nb | Disadvantages of doping with Nb | Catalytic process | Ref. |
|---|---|---|---|---|
| V-O | Increases de number of acid sites. | Formation of $VNbO_4$ and $VNbO_5$ phases, which are detrimental and decreases the number of V active centres | Propane ODH | [16] |
| Mo-V-O | Induce the formation of Mo–V–O mixed phases<br>Prevents the formation of $MoO_3$ and $V_2O_5$ | | Ethane to acetic acid<br>Ethane ODH | [44]<br>[2] |
| Ni-O | Favours the diffusion of ethylene | Can form $NiNb_2O_6$ structure that is detrimental | | [24–25] |
| Mo-V-Te-O | M1, rutile $VSbO_4$ and/or M2 phases are able to incorporate small amounts of $Nb^{5+}$, improving the stability of the structure and the site isolation of active centers. | | Propane to acrylic acid | [48,49] |
| Sb-V-O | V–Nb–O bonds improve selectivity | Formation of unselective $SbNbO_4$. | Propane to acrylonitrile<br>Glycerol to acrylonitrile | [55–58]<br>[70] |
| V-P-O | Nb initiates local disorder promoting VPO rearrangement into the stable active phase during reaction in significantly less time<br>Increases mechanical strength | | Butane oxidation to maleic anhydride | [73] |

properties and increase acidity, rendering systems more efficient for selective oxidation or ammoxidation reactions. Niobium also promotes catalytic performance by promoting entanglement of other elements in mixed oxide catalysts, and preventing the build up of segregated pure phases, e.g., in the Mo–V–O system, M1 phase, or the rutile $VSbO_4$ system. The ability of niobium to coordinate with many elements promotes such entanglement, and must also account for higher structural reactivity that significantly shortens required by VPO catalysts to attain steady state operation; such a time is due to structural rearrangement, significantly enhanced by niobium. The promoting effect of niobium additive is limited to low loadings, and typically, is lost when well defined niobium-containing phases form.

Table 1 summarizes the most representative applications of niobium as a doping agent for selective oxidation reactions with mixed oxides catalysts. It briefly comments the advantages and limiting conditions. This is a general vista, since the properties depend on the preparation procedure and on the precursors that are used to prepare the catalyst.

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