



The fascinating effect of niobium as catalytic promoting agent

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This paper is dedicated to Prof. Maria Ziolek on the occasion of her 70th birthday.

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ABSTRACT

Niobium is a very important element in catalysis, active component of many catalytic systems. But it is not only a major component in many catalytic systems; in addition, it is usually used as a key promoter, because it has a rich complex chemistry and is able to react with many elements forming a wide range of compounds and oxide phases with complex structures. Thus, present contribution makes a brief review on the main industrial catalytic processes in which niobium has been used as a promoting agent during the last decade. The uses of niobium as main component in the catalytic formulations have not been considered.

1. Scope

Niobium is an important element, used for the preparation of several catalytic materials, and its catalytic properties have been analyzed [1–3] extensively for both heterogeneous and homogeneous [4] applications. But it is not only used as main component in catalytic formulations, or as support as Nb₂O₅, since it is also usually used in a small amount in the formulation of several catalytic systems, as additive. Ten years ago our group published a review paper about the promoting effect of Nb as additive for catalysts formulations [5]; with the objective of investigating the promoting effect of Nb on different catalytic formulations used for selective oxidation reactions. It was shown that there were four main types of selective oxidation reactions in which Nb was used as promoting agent of the catalysts: oxidative dehydrogenation of lower alkanes (ODH) to produce olefins, oxidative coupling of methane and oxidation and ammoxidation of alkanes to produce oxygenates and nitriles. It was shown (5) that the promoting effect is mainly due to the ability of Nb to combine with many other elements forming new compounds. Upon such interaction, typically the redox properties are modulated, and increase the acidity, rendering systems more catalytically active. Nb also enhances the catalytic performance to active phases by promoting the entanglement of other elements in such active phases that must change the oxidation state under reaction conditions. It seems that such entanglement favors the necessary structural changes that the active phase must suffer under reaction conditions. It also prevents the buildup of segregated pure phases, e.g., in the Mo–V–O system, M1 phase, or the rutile VSbO₄ system. This promoting effect of niobium additive is limited to low loadings, and typically, is lost when well defined niobium-containing phases form.

A brief analysis of literature during the last decade in selective gas-phase oxidation heterogeneous catalysis, shows that the interest in the

eighties-nineties was focused in the synthesis of oxygenates, nitriles and olefins [6], and, although these applications have continued to develop until today, the research efforts on environmental catalysis are receiving more interest [7], and also this tendency is detected for those studies that use catalytic materials in which Nb is used as dopant, as will be shown in the present contribution. Thus, the objective of this work is to update the previous one of 2009 (5), in order to evaluate and analyze the use of Nb as an additive in the formulation of catalysts for partial oxidation reactions. Therefore, a review of the bibliography on this issue, Nb as additive of mixed-oxide catalysts for redox reactions, during the last decade in this field is presented.

2. Propane and ethane ODH

The oxidative dehydrogenation (ODH) of propane and ethane [8–10] is a promising route for olefins production due to the favorable thermodynamic and kinetic advantages that it has compared with conventional thermal cracking, but it has some difficulties in the control of the selectivity due to over-oxidation side reactions that increase the selectivity to CO and CO₂. Several catalytic systems have been tested and have demonstrated to be promising for the ODH of both ethane and propane. By 2003, Tanabe (2) already reviewed the promoting effect of doping Mo–V–O catalytic system with Nb, and this multioxide catalytic system is still considered one of the most promising for the commercial implementation of this process [11–13]. And, by 2009 (5), it was shown that Nb had shown a promoting effect on several catalysts for both ethane and propane ODH reactions, such as VOx supported and NiO catalysts. In all cases, it was shown that when a small amount of Nb cations were able to incorporate in the lattice, modifying the acidity and redox properties, the catalytic properties were enhanced, on the contrary, a high Nb content led to saturate

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the bulk lattice sites and to the formation of non-selective Nb containing mixed oxides, such as NiNb_2O_6 , VNbO_4 or VNbO_5 .

A brief analysis of the literature during the last ten years shows that these catalytic systems (Mo-V-O, NiO and VOx supported) are still being investigated for ODH of propane and ethane, and the effect of Nb, as dopant, is still being studied as promising catalytic systems. NiO catalytic system was reported as active and selective for ethane ODH by Lemonidou and coworkers [14,15], among others [16], and it was described the enhancing effect of Nb as dopant, since pure NiO presented a quite low ethylene selectivity during ODH reaction, whereas 90% ethylene selectivity with high activity was reported for a $\text{Ni}_{0.85}\text{Nb}_{0.15}\text{O}_x$ mixed oxide catalyst (15). This Nb promoting effect was studied by our group by *operando* Raman spectroscopy [17,18] and HRTEM [19] in order to characterize the active species under real reaction conditions. These results showed that two Ni-Nb-O phases can be form in these catalysts, a Nb-poor phase with a particle size in the 20–50 nm range, and a Nb-rich one, with a smaller particle size. The Nb-rich phase is not catalytically active for alkane activation reactions, in line with other studies by other groups [20,21]. In this line a study by Lemonidou and coworkers [22] showed the similarities and differences between NiO and Nb doped-NiO catalysts during alkane ODH and pointed out the formulation $\text{Ni}_{0.85}\text{Nb}_{0.15}\text{O}_x$ as optimum catalyst. The study showed similar active sites for alkane activation, but they could identify a surface concentration correlation of O- species with Nb content, that was attributed to a less activity in the activation of alkane and subsequently a higher selectivity towards the olefin (22). The redox properties of Ni-Nb-O catalysts were evaluated by CO oxidation for various Nb contents [23], they reported less activity for the samples with higher Nb contents, in line with the previous studies that indicated the Nb-poor phase as the most catalytically selective.

In the case of Nb as dopant of V-containing catalysts, it was reported (5) that Nb enhances the catalytic properties of vanadium catalysts for propane oxidehydrogenation only when it does not form mixed V-Nb-O phases, being this enhancement of the catalytic performance related with the acidic properties of niobium. During the last decade, a few papers have continued investigating this promoting effect of Nb for alkane ODH reactions on Vanadium containing catalysts. For example, Hossain et al [24] investigated the effect of VOx-Nb formulations supported on La stabilized Al_2O_3 support for the oxidative dehydrogenation of ethane. They founded higher ethylene selectivity and ethane conversion for the Nb-doped catalyst. They attributed this effect since Nb was able to minimize the formation of crystalline V_2O_5 phases for the same vanadium contents, being this oxide undesirable for ODH reaction since it favors total oxidation reaction. The isomorphic substitution of V atoms in Nb_2O_5 crystals was studied by Ramalho and coworkers [25], that reported the oxidative dehydration of glycerol into acrylic acid on V/ Nb_2O_5 supported catalysts. According to their theoretical calculations, they suggested that the incorporation of V is more favorable in the Nb_2O_5 bulk structure than on the surface. They related this change in the lattice with the lower energy during some steps of the reaction mechanism, though a thermodynamic analysis. Although according with their findings the incorporation of V in the catalysts formulation does not introduce any changes in the mechanism, it changes the reaction energetics, favoring the occurrence of some steps, and increasing the reaction rate, according with previous studies (5) that also pointed out the enhancing effect of the presence of some Nb–V–O bonds in the catalysts, without the formation of crystalline V–Nb–O structures.

During the last decade, some groups have focused in the design of synthesis methods for the preparation of nanoscaled catalysts, which means that the procedure allows to control not only the chemical composition of the catalysts (active phases that are on the surface), but also the morphology of the catalytic material, since submicrometric and submicronanoscaled materials present several advantages with respect to conventional ones [26,27], with this methods, highly active and selective nanocatalysts have been described [28,29]. In this line, the

synthesis of NbOx/CeO₂-rods catalysts by hydrothermal method, and their use for propane ODH was reported [30]. They reported that the presence of Nb species on the surface of the CeO₂ was able to decrease the surface reducibility of CeO₂ rods, leading to an increment in the propene selectivity at the same conversion range but, decreasing the activity at the same temperature. Similar results were achieved by our group, since it was reported the synthesis of sub-micron diameter fiber VOx/ZrO₂ catalysts by electrospinning for propane ODH reaction (26) and reported that the presence of Nb sites decreased the activity [31]. This in line also with the results reported in the previous paragraph for the NiO catalytic system, for low Nb concentration, both selectivity and activity were increased due to the presence of a Nb-poor phase, identify by Raman spectroscopy (19), and subsequently, for high Nb concentration, a different phase was detected, being detrimental for alkane ODH reactions.

Another important group of materials that are promising catalysts for alkane ODH reactions are those based on mesoporous molecular sieves. These materials are attractive catalytic supports since they have an ordered structure that allows them to disperse oxide active phase species. Ziolk et al [32] demonstrated that the surface hydroxyls groups of mesoporous MCM-41 type materials are able to disperse vanadium mixed oxide species, being more convenient that conventional oxide supports such as silica. Ziolk group investigated the incorporation of Nb species to these mesoporous materials (MCM-41 and SBA-15) [33–38]. However, for Si/Nb ratio 32 or 64, in most cases Nb was located not only in the walls of mesoporous channels, but also in the extra framework sites, as Nb-oxides phases. It was demonstrated that the efficiency of Nb species incorporation during the synthesis procedure depends on the structure of the final material and it is much higher for MCM-41 (33) than for the SBA-15 (35). The most important differences in the synthesis procedure of these two types of mesoporous molecular sieves are the type of template used (ionic surfactant for MCM-41 and triblock copolymer in case of SBA-15) and the synthesis medium (basic, MCM-41 and acidic, SBA-15). Another important parameter to be considered is the Nb precursor, which also influences the amount of metal included into the mesoporous material [39]. Ziolk group described by the first time the preparation of Nb-Si mesostructured solids avoiding extra framework Nb-oxide species [40], as was confirmed by XRD and UV–vis, and demonstrated that these materials were promising for ethane ODH reaction. The absence of extra framework Nb species in these materials was an advantage because the presence of Nb outside the walls caused the increase of alkane total oxidation reaction to COx, decreasing the selectivity to the olefin (40). This was evidenced by the catalytic results during ODH reaction described by Ziolk group (Table 1) for the three types of mesostructured materials (NbMCM-41 and NbSBA-15, with extraframework Nb species and NbSBA-3 without), that evidence that Nb tetrahedrally coordinated and connected with siliceous-oxygen species in the walls is responsible for the propane ODH reaction towards propylene, whereas niobio-oxide species located in the extra framework sites are responsible for the total oxidation towards CO and CO₂. Due to the homogeneity of Nb species in these catalysts, it was possible to establish the correlation of the activity and selectivity with

Table 1
Activity for ODH of propane at 813 K (after 1 h time on steam) (Reproduced from Ref. [40]).

Catalyst	Real atomic ratio Si/ Nb	Propane conversion (%)	References
NbSBA-3-32(Co)	113	9.8	[40]
NbSBA-3-32(Cl)24	24	15.3	[40]
NbSBA-3-64(Cl)52	52	9.8	[40]
NbSBA-3-128(Cl)	107	13.8	[40]
NbSBA-15-32(ox)	73	2.8	[35]
NbSBA-15-128(ox)	207	7.4	[35]
NbMCM-41-32(ox)	26	6.6	[33]

the number, strength of active sites, as well as the isolation of Nb species.

3. Selective (am) oxidation of light alkanes to nitriles and oxygenates

Amoxidation (oxidation with O₂ in the presence of NH₃) of light alkanes, such as ethane and propane, is a promising process for the production of nitriles, such as acrylonitrile (from propane) [41,42] or acetonitrile (from ethane) [43]. The partial oxidation of light alkanes to obtain oxygenates with commercial interest, such as acrylic acid have been also investigated during the last ten years. These reactions share similarities that result in different catalyst requirements. The key difference with respect the alkane used as starting material is that all C–H bonds in ethane are equivalent and primary, whereas propane also has also a secondary carbon –CH₂–, a methylene group. Thus, the activation of the alkane (ethane or propane) requires different active sites [44], being Ni-Nb-O catalysts able to catalyze both, whereas other studied catalytic systems, such as multioxide Mo-V-Nb-Te-O or Sb-V-(Nb)-O, are only able to activate the propane, and not active for the ethane based reaction (44). In all cases, the Nb species roles a crucial play in the catalytic behavior, as have been already described in the previous section for NiO based catalysts, in which a low content Nb doped NiO phase was identified as active for these partial oxidation reaction (19). The role of Nb in the activity behavior and characterization of Sb-V-(Nb)-O catalytic materials was already described in the previous review paper (5). With respect the multioxide (Mo-V-Nb-Te-O) based catalysts, there are several studies on the role of Nb content on the structure and activity of them [45,46] that have been performed during the last decade. In this catalytic system it has been described the structure of the active phases, that has been named as M1 [47,48]. The promoting effect of Nb is only positive at low Nb contents [49–51]. Millet et al [52] analyzed the cationic and valence distributions in the M1 phases of catalysts with different Nb compositions using several techniques such as V K-edge and Sb or Te L₁-edge XANES spectroscopy. They concluded that Nb modulates the surface acidity and the amount of Mo⁵⁺ species of the M1 phase, and by this way it can be inhibit the over-oxidation of the desired product (oxygenate such as acrylic acid).

Ziolek team worked on describing also Nb-doped mesoporous materials with catalytic applications in these (am)oxidation of light alkanes processes. They described Nb containing MCM-41 and MCM-48 materials as support for VOx species during propane amoxidation reaction [53]. Table 2 reproduces the activity data that they reported (53). In this paper it was shown that for high V + Sb coverage on the corresponding support, MCM-48 type support was able to stabilize Sb_{0.95}V_{0.95}O₄ rutile structure, in which V is in a reduced oxidation state [54,55], whereas MCM-41 type supports favored the formation of

Table 2

Activity results reproduced from (53) during propane amoxidation reaction at 773 K.

Catalyst	Propane conversion (%)	Selectivity (%)				
		Acrylonitrile	Acetonitrile	Acrolein	Propene	COx
MCM48	1.7	1.6	28.6	8.7	61.1	–
0.5VSbNb/MCM48	18.8	58.0	19.3	2.3	16.8	3.6
1VSbNb/MCM48	23.9	67.8	14.7	2.9	9.8	4.8
MCM41	1.1	–	40.3	–	48.5	11.2
0.5VSbNb/MCM41	6.4	15.2	13.6	17.7	46.9	6.6
1VSbNb/MCM41	11.7	21.8	20.9	5.7	42.9	8.2
NbMCM41	3.0	14.9	63.6	–	20.2	1.3
0.5VSb/NbMCM41	17.8	29.2	37.8	9.4	19.8	3.8
1VSb/NbMCM41	18.6	20.7	38.3	3.0	20.3	17.7
AlMCM41	4.5	–	64.0	–	31.2	4.8
0.5VSb/AlMCM41	4.9	4.6	11.3	2.9	57.3	23.9
1VSb/AlMCM41	3.2	0.9	5.0	0.5	83.8	9.8
1SbV/NbMCM41 I	7.8	30.3	22.8	1.7	41.2	4.0
1SbV/NbMCM41 II	11.8	27.3	33.8	3.0	33.7	2.2

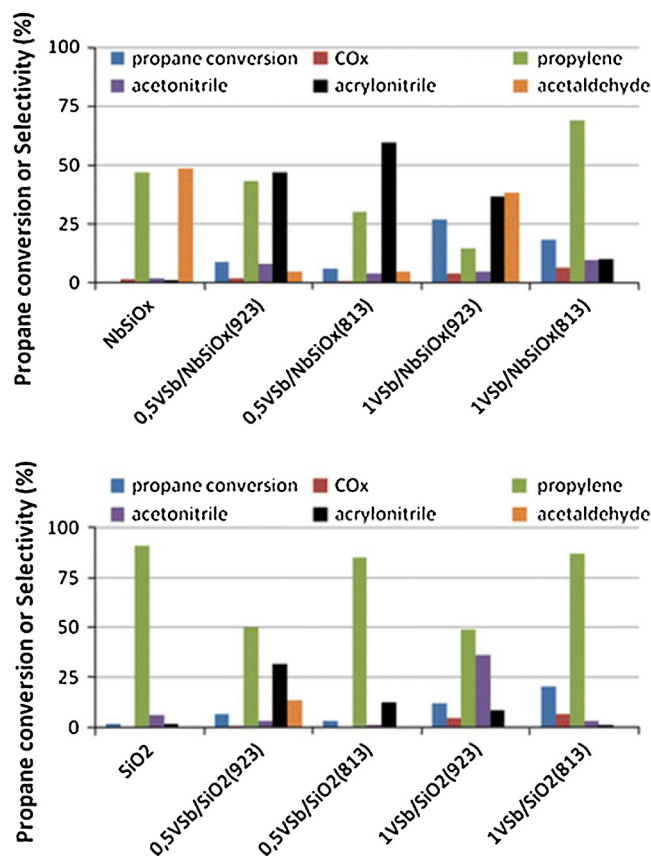


Fig. 1. Propane conversion (%) and selectivity to main products (%) obtained during the propane amoxidation reaction at 773 K. Reaction conditions: total flow 20 cm³ min⁻¹; feed composition (% volume): C₃H₈/O₂/NH₃/He (9.8/25/8.6/56.6), 100 mg of Catalysts. Reproduced with permission from (56).

oxidized Vanadium 5+ species, detrimental for the partial oxidation reaction. It was also described that when Nb was introduced during the synthesis of MCM-41 support, the surface acidity of such Nb-doped material was able to influence the catalytic behavior during the amoxidation reaction. In all cases, Nb sites were able to interact with V and to stabilizing rutile active phase, and increasing the selectivity to nitriles formation.

Ziolek team also described a Niobiosilica material that demonstrated to be a good catalytic support also for the Sb-V-O active species [56], in this case, they described a synthesis method for a non-ordered porous niobiosilica material, without the use of a template, and the use

of such material as support for VO_x active species during the propane ammoxidation reaction. Fig. 1 shows the activity results obtained in such work. It can be observed that in absence of V sites, the catalysts are not selective for nitrogen insertion. For all the Sb–V catalysts, the selectivity to acrylonitrile increases with the use of the Nb-containing support, being higher for the catalysts with lower coverage. In this case the Nb promoting effect is related to the formation of larger particles of rutile VSbO₄ phase, as identified by XRD (56), that have structural defects in the structure, which enhances the catalytic properties. This results are in line with previous studies on ammoxidation over Sb–V–O catalytic system that showed that the SbVO₄ rutile structure stabilizes cation vacancies in its structure [57], and with the ability of Nb species to incorporate into the rutile lattice [58]. This leads to a higher structural reactivity that significantly enhances the catalytic properties of the rutile SbVO_x active phase for propane ammoxidation. Since the promoting effect of niobium additive is limited to low loadings, and typically is lost when well defined niobium-containing phases form, it is necessary to control the amount of Nb to be incorporated, and this is possible using the Nb-doped catalytic supports described by Ziolek group (53,56).

4. Oxidation of CH₄

Gas natural transformation into hydrogen and chemical intermediates has been the objective of several studies during the last decades, being one of the most studied the transformation of methane into syngas. At industrial scale it is carried out through steam reforming, being the partial oxidation of methane a good alternative that is being studied [59,60]. One of the disadvantages of the steam reforming process ($\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$) is that it is endothermic, whereas partial oxidation ($\text{CH}_4 + 1/2\text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2$) is exothermic and in addition it presents a $\text{H}_2/\text{CO} = 2$ ratio, which allow the straightforward transformation for obtaining methanol or Fischer-Tropsch processes [61]. Good results for the methane partial oxidation have been obtained with noble metals based catalysts [62], although Ni-based also present promising results [63] with the advantage of the low cost in comparison with noble metal based materials. Also in the case of reactions that involve the activation of alkane C–H bonds, Nb compounds are quite promising, since DFT calculations as well as the experimental evidences have demonstrated the ability of Nb–O bonds to initiate the activation of such bond [64–66]. Although that, as have been already presented in the previous section, Nb, at low concentration, is able to improve the catalytic properties of NiO based catalysts for the partial (am)oxidation of ethane and propane, thus, supported NiO/Nb₂O₅ and bulk Ni–Nb–O catalytic system have been also investigated for the partial oxidation of methane.

A recent paper by Brandao et al. [67] describes the promotion effect of Nb species in Ni based catalysts for this process. They prepared two series of catalysts, one in which Nb₂O₅ was used as support for NiO species, and a second series of perovskite based materials with compositions LaNi_(1-x)Nb_xO₃ ($x = 0, 0.5$). It was described (67) that the presence of Nb in the perovskite based catalytic materials increased the activity close to 20% weight of nickel. They attributed this results to a better dispersion of Ni active sites, but in this study Raman spectroscopy was not used in order to confirm the presence of the Ni–Nb–O mixed phases already described (18,19). For a high amount of Nb in the catalytic formulation, as in the case of the Ni⁰/Nb₂O₅ catalyst studied in the paper (67), no syngas formation was detected. This was attributed to a strong metal support interaction suppressing the accessibility of Ni⁰ to the reactant gases and allowing only total oxidation.

5. PROX

CO Preferential oxidation (PROX) is used for removing small amounts of CO to trace level from the hydrogen-rich stream, which will be then supplied as a fuel to PEM (polymer–electrolyte membrane) fuel

cells. The key to the application this reaction is to develop an appropriate catalyst that operates well in a wide temperature window and has good resistance to CO₂ and steam [68]. There are some catalytic systems that have demonstrated to be promising for the commercial implementation of this process, being supported noble metals, specially Pt (68) and Au [69,70], and Ce-based catalysts [71,72], that have demonstrated good results. The combination of both has also been investigated (Pt supported on CeO₂ based materials). Ramos-Fernandez and coworkers [73] prepared Pt supported on CeO₂–TiO₂ supports, and demonstrated that these catalysts presented a better performance in comparison with Pt supported on pure oxides. The effect of Nb sites on the reaction mechanism of this process has been also investigated. The adsorption of CO on the catalytic active sites was studied by Oliveira et al. [74] by in situ IR absorption spectroscopy, that showed how the presence of substituting Nb atoms in the structure of a hematite catalytic material modifies the surface properties. As a result, the presence of Nb changes the catalytic properties by the addition of oxygen vacancies. In addition, mixed oxides containing Nb, such as CeO₂–Nb₂O₅ mixtures, have demonstrated also good results as support for Pt particles for preparing PROX catalysts. Sepúlveda-Escribano and coworkers investigated the effect of Nb content in these materials [75]. It was found that the Pt/Nb₂O₅ catalyst was almost inactive during the PROX reaction, whereas Pt/0.7CeO₂–0.3Nb₂O₅ sample achieved a quite high CO conversion (85%) with a high selectivity, as in the case of other catalytic systems doped with Nb that have been described in the present review paper, a solid solution containing Nb was identified. It was described that Nb⁵⁺ is able to diffuse into the CeO₂ lattice to replace some Ce⁴⁺, and was described also that these changes on the structure of the support affects the oxide surface and morphology of the Pt nanoparticles, improving their catalytic activity.

6. Environmental applications

Both oxidation and reduction processes found many applications in environmental catalysis (7), some well known examples are the selective catalytic reduction (SCR) for removal of oxides of nitrogen (85), desulfurization [76], including the selective oxidation of H₂S to elemental sulfur [77,78], removal of N-containing organic pollutants [79,80] and removal of VOCs by total oxidation [81–84]. Most of the catalytic systems that have demonstrated to be effective for these redox processes are those based in mixed oxide materials, being also in this case Nb a promoting additive for them.

A very important environmental issue that catalysis science must face is the abatement of harmful compounds such as nitrogen oxides (NO_x), from both mobile and stationary sources. During the last decade, more efforts have been focus in the development of catalytic converter technologies for diesel-powered vehicle engines that operate at high air/fuel ratios, since “three-way” catalysts have been successfully used in gasoline vehicles for over 30 years to control the emissions of CO, hydrocarbons and NO_x. In this way, several techniques seem to be feasible for NO_x abatement, being one of the most promising the ammonia- or urea- Selective Catalytic Reduction (NH₃-SCR) [85]. Different catalytic materials have been described as active and selective to this process, with active phases such as Cu- and Fe- based catalysts [86,87], Mn–Ce–O mixed oxides [88,89], and V based [90]. Ceria, and Ce–Zr–O based catalysts constitute the most promising for this process, due to the redox cycling between Ce³⁺ and Ce⁴⁺, that has been also used for three-way catalysts (TWCs) [91–94].

Several groups have investigated the effect of Nb as dopant for these catalytic systems for the SCR reaction, due to the acid properties of Nb sites. Since for the SCR reaction a mechanism with two active sites, in which both redox and acid functionalities are required [95] has been proposed, it makes sense the combination of Nb (acid properties) and Ce (redox properties). Ce–Nb–O catalytic materials have been reported as active and selective for the SCR of NO_x, urea hydrolysis and soot oxidation in diesel exhaust [96], demonstrating the importance of

Table 3

Main applications described during the last decade of Nb as doping agent during redox reactions with bulk and supported mixed oxides.

Catalytic System	Advantages using Nb	Disadvantages of doping with Nb	Process	Ref
Ni-Nb-O	Nb-poor phase may form, enhancing catalytic properties.	Nb-rich phase is not catalytically active	ethane ODH ethane ammoxidation	[17–22]
Nb doped- VOx /support Nb/MCM41 Nb/SBA-15	Acid sites enhances catalytic activity. Acid sites enhances catalytic activity. Nb sites doped in the support stabilize the supported active phases.	Mixed V-Nb-O crystalline phases detrimental Extra framework NbO is detrimental	propane ODH ethane ODH Propane ODH Propane ammoxidation propane ammoxidation	[5] [33–38] [53] [5]
Sb-V-Nb-O	Acid sites enhances catalytic activity. Nb creates vacancies in the VSbO ₄ rutile active phase.	Mixed V-Nb-O or Sb-Nb-O crystalline phases are detrimental	propane ammoxidation	[45–52]
Mo-V-Nb-Te-O	Acid sites enhances catalytic activity. Nb creates vacancies in the M1 active phase		methane partial oxidation PROX	[67] [73]
Ni-Nb-O Pt/Ce-Nb-O Ce-Nb-O Ce-Zr-Nb-O	Nb at low contents enhances activity Nb creates vacancies in the CeO ₂ lattice. Acid sites enhances catalytic activity. Good behaviour during deactivation processes.	Nb at high contents is detrimental Pure Nb ₂ O ₅ support makes Pt/Nb ₂ O ₅ inactive. Nb at high amount creates a deficit of active sites, being detrimental.	SCR	[96–105]

having both types of active sites in order to have appropriate catalysts. In addition, the Nb-Ce-O catalysts showed a good behavior against the most significant deactivation processes (hydrothermal ageing and sulfur poisoning). Gao and coworkers [97] investigated the effect of Nb as dopant of Ce-based catalysts for the SCR reaction, in order to establish relationships between the structure and activity of them. They synthesized a series of Ce-Nb binary oxides with different compositions, and found several conclusions. First, Nb atoms, are able to incorporate into the cerium oxide lattice resulting in materials with larger surface areas compared with CeO₂ single oxide, which is beneficial for the catalytic behavior, since more active sites are provided. Pyridine adsorption experiments (97) demonstrated that the introduction of Nb species to CeO₂, led to an enhancement of the number of acid sites on the samples. Nb–OH bonds can serve as Brønsted acid sites, whereas Nb=O bonds as Lewis ones. At low temperatures, both Brønsted acid sites and Lewis acid sites may contribute to the reaction, whereas only Lewis acid sites are responsible for the reaction at high temperatures. These effects, increase of acidity, of surface adsorbed oxygen and the changes on the chemical environment of Ce sites, due to the incorporation of Nb, give rise to a higher catalytic performance for the SRC reaction. Wu et al. [98] studied the effect of Nb on CeO₂-ZrO₂ mixed catalysts. Quite good results were obtained with a Ce-Zr-O sample containing 15% wt of Nb₂O₅, in this case, 100% selectivity to N₂ was obtained. As in the case of previous works with CeO₂, also for Ce-Zr-O, it was shown how the Nb incorporation promoted the formation of Ce³⁺ ions, oxygen vacancies and active oxygen species, resulting in a better catalytic performance.

In addition to Ce-Zr-O based catalysts, other materials have been also described as promising for the SCR reaction, as for example the V₂O₅/TiO₂ based catalysts [90,99–102]. Nb has been also described as a good dopant for V supported TiO₂ catalysts. During the SCR reaction, it is also important to consider the sulfur resistance of the catalysts, since NH₄HSO₄ would be inevitably produced through the reaction of certain amounts of SO_x, H₂O and NH₃ in the exhaust gases that are treated by the SCR process. The as-formed NH₄HSO₄ blocks the pore structure, covering the catalytically active sites, rendering a negative effect on the SCR reactions and constituting the main barrier in commercializing low-temperature SCR systems [103]. In this sense, Gao et al [104,105] investigated the effect of Sb and Nb on V based catalysts during the SCR reaction, in order to increase the sulfur resistance of the catalysts. They found that for high Nb and Sb amounts, it might result in a deficit in TiO₂ sites for the accommodation of the reaction intermediate NH₄HSO₄, causing the appearance of crystallite ammonium sulfate salts, and decreasing the activity. As have been described in this work for other catalytic systems and reactions, the promoting effect of Nb is lost at high concentrations. But, for low Nb or Sb contents, the electron density around S atom have a positive effect on the reaction

mechanism, promoting the decomposition of intermediate NH₄HSO₄ and enhancing the sulfur resistance of the catalysts. Nb has also demonstrated to be a good dopant in other catalytic systems usually used for SCR, as in the case of zeolite based [106]; also in this case the addition of small amount of Nb improved the oxidation ability, created vacancies, and increased the poison resistance of the catalytic materials at high temperatures.

7. Concluding remarks

Group five elements are a group of metal transition elements that have a rich chemistry and properties [107–110] that makes them very useful in catalysis. Niobium has an invaluable additive due to its ability to introduce in crystalline lattices creating vacancies (that usually enhances the catalytic activity), and due to its acidify, since the increase of surface acidity may render in an enhancement of the active sites for adsorption in some cases, that increases the reaction rate. Due to these main properties, upon its interaction, it typically modulates redox properties of the active phases and increases the number of active sites, and resulting in a catalytic material more efficient for redox reactions.

Table 3 summarizes the most representative applications of Nb as doping agent of catalytic systems for some redox reaction of industrial interest that have been studied during the last decade. This is quite a brief resume to get some trends, but it should be considered that the catalytic properties depend on many factors, such as the preparation procedure and on the precursors that have been used in each case. The main conclusions are similar to those described in the revision made in 2009 (5), that the Nb enhancing effect is lost at high Nb concentrations, due to two main reasons: when it forms crystalline structures, they are not active and some other elements (such as V, Ni or Ce) are not available to form the active-phase when they are bond to Nb forming such structures. In addition, it seems that moderate activity in most cases increases the reaction rates, but when the number of acid sites is high, it usually causes that the reaction products are not able to desorb and the selectivity to over-oxidation products (CO_x) increases. Thus, Nb is a good additive for both oxidation and reduction processes catalyzed by metal oxides, but it has to be incorporated at low amount in most of the cases.

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