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On the Redox and Catalytic Properties of Promoted NiO Catalysts for the Oxidative Dehydrogenation of Ethane

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Abstract

NiO and metal promoted NiO catalysts (M-NiO, with a M/(M+Ni) at. ratio of 0.08, being M= Nb, Sn or La) have been prepared, tested in the oxidative dehydrogenation (ODH) of ethane and characterized by means of XRD, TPR, HRTEM, Raman, XPS and in-situ XAS (using H_2/He, air or C_2H_6/He mixtures). The selectivity to ethylene during the ODH of ethane decreases according to the following trend: Nb-NiO ≈ Sn-NiO > La-NiO > NiO, whereas the catalyst reducibility (determined by both TPR and XAS using H_2/He mixtures) shows the opposite trend. However, different reducibility and catalytic behavior in the absence of oxygen (ethane/He mixtures) have been observed, especially when comparing Nb- and Sn- promoted NiO samples. These differences can be ascribed mainly to a different phase distribution of the promoter. The results presented here are discussed in terms of the nature of active and selective sites for ODH of ethane in selective and unselective catalysts, but also the role of promoters and the importance of their phase distribution.

1. INTRODUCTION

Ethylene, which is mainly obtained via steam cracking, is the most important building block in Petrochemistry with a worldwide production in 2015 of ca. 150 million ton.[1,2] However, steam cracking is one of the most energy-demanding processes in the chemical industry. For this reason, and in order to cope with the increasing demand of ethane, new alternative processes for its production have been proposed in the last decades.[3-8] Among all of the alternatives, including the production of bioethene,[3-5] the oxidative dehydrogenation (ODH) seems to be the most promising one, with a view to a future industrial application,[6-8] especially after the development of very active and selective catalysts working at moderate temperatures; i) MoVTeNbO mixed oxides, with yields of ca. 75%; [9,10] and ii) NiO-based catalysts with yields of ca. 40%.[11]

In the case of NiO-based catalysts, at least three different types of catalytic systems have been suggested after the pioneering work of Lemonidou et al.[11, 12]: i) Me-promoted catalysts,[11-25] especially Nb- [11-20, 23-25] and Sn-promoted [21-24] NiO (with Ni-content higher than 80 wt% of NiO); ii) Diluted NiO, using porous clay heterostructures (with Ni-content of ca. 20-50 wt%);[26] and iii) Supported NiO, as NiO/Al_2O_3 materials (with Ni-content of ca. 5-10 wt%).[27-30] Nb- and Sn- promoted NiO are among those based on nickel oxide the most selective catalysts to ethylene in the oxidation of ethane. In fact, yields to ethylene higher than 40% have been reported. These high yields are more due to the stability of the ethylene formed in the oxidation of ethane than to a high initial selectivity to ethylene at ethane conversions close to zero.

Nevertheless, the nature of active and selective sites in NiO-based catalysts is still controversial. In this way, it has been proposed that the nature of surface sites in promoted NiO catalysts can be strongly modified by considering acid characteristics of the metal oxide promoters.[23] In addition, the morphology of NiO particles could play an important role on the selectivity to ethylene,[24] as a consequence of a higher distortion of the NiO crystal lattice parameter.[26] Recently, the redox kinetics of several NiO-based oxygen transfer materials (OTMs) supported on different oxides have been studied. Interestingly, the nature of the supports highly influences the redox kinetics which is directly related to the different strength of metal-support interactions.[31]

In this work, we aim to shed light on the reduction and oxidation steps during the catalytic cycles in the oxidative dehydrogenation of ethane on modified NiO catalysts. Thus, we have studied unpromoted and metal-promoted NiO catalysts (with a Metal/Ni atomic ratio of 12; and Me= Nb, Sn or La), prepared by the same method, by combining in-situ XAS at the Ni K-edge under different atmosphere (in the presence and absence of O_2 in the feed) with catalytic and temperature-programmed reduction experiments. In addition, fresh and used catalysts have been characterized by X-ray diffraction, electron microscopy and Raman and XPS spectroscopies. The effect of both reduction-reoxidation kinetics and phase distribution of the promoter in the catalytic performance is also discussed.

2. EXPERIMENTAL METHODS

2.1. Catalyst preparation

Unpromoted NiO catalysts were prepared through the evaporation at 60ºC of a stirred ethanolic solution of nickel (II) nitrate and oxalic acid, considering an oxalic acid/Ni molar ratio of 1. The La-, Nb- and Sn-promoted NiO catalysts were prepared similarly by including also the corresponding salts (SnC_2O_4 for Sn, ammonium niobate (V) oxalate for Nb and lanthanum (III) oxalate hydrate for La) in the synthesis gel. The amount of promoter has been fixed in X/(X + Ni) atomic ratio of 0.08, which is close to the optimal value for attaining the highest selectivity to ethylene. All solids were dried overnight, at 100ºC, and finally calcined for 2 h at 500ºC (in static air).

2.2. Catalyst Characterization

Surface areas of the catalysts were determined by multi-point N_2 adsorption at −196°C on a Micromeritics TriStar 3000 apparatus, treating the data in accordance with the BET method.

Powder X-ray diffraction (XRD) were collected in a PANalytical X'Pert PRO diffractometer (with a monochromatic CuKα1 source), which was equipped with a X´Celerator detector in a Bragg-Brentano geometry.

Scanning-Transmission electron microscopy (STEM) images were collected in a JEOL JEM-2100F field emission gun microscope operating at 200 kV, which was equipped with a High-Angle Annular Dark-Field (HAADF) detector. Energy-Dispersive X-Ray Spectroscopy (EDS) analyses were also performed using a coupled X-Max 80 (Oxford Instruments) detector.

Temperature-programmed reduction (H_2-TPR) experiments were carried out in a Micromeritics Autochem 2910 equipped with a TCD detector, in which the reducing gas was 10% H_2 in Ar (total flow rate of 50 ml min^{-1}). The samples were heated from 40 to 800°C at a heating rate of 10 °C min^{-1}.

Raman spectra well recorded in an inVia Renishaw spectrometer, using and exciting wavelength of 514 nm and a power on the sample of about 15 mW. The spectrometer is equipped with a Renishaw HPNIR laser and an Olympus microscope.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Physical Electronics spectrometer (PHI 500) with scanning non-monochromatic X-ray Mg Kα radiation (300 W, 15 kV, 1253.6 eV) as the excitation source.[26]

In-situ time-resolved XANES experiments (Ni K-edge spectra) were recorded in transmission mode, using an in-house cell developed BM25-SpLine beamline at the European Synchrotron Radiation Facility, which can work under selected atmosphere until 700º C. Mass flow controllers were used to introduce gases into the cell. Samples for XAS analysis were prepared weighting the optimum mass amount for maximizing signal-to-noise ratio ($\mathrm{Ln}(I_0/I_1) \approx 1$), which was diluted in boron nitride and pressed into pellets. All the spectra were acquired at a time resolution of approximately 3 min/spectrum, in the range 8200-8490 eV and their normalization and linear combination fitting (LCF) were carried out with the software Athena. Calcined samples and metallic Ni were used as references in the LCF calculations.

2.3. Catalytic tests

The catalytic experiments were carried out in a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm), at atmospheric pressure, in the temperature range 350–450ºC. The feed consisted of a mixture of $C_2H_6/O_2/He$ with molar ratios of 5/5/90 or 5/0/95. Several catalyst weights (from 0.05 to 5.0 g) and total flows (from 20 to 150 ml min^{-1}) were studied. Catalyst samples were introduced into the reactor diluted with silicon carbide in order to keep constant volume in the catalytic bed. Reactants and products were analyzed by gas chromatography, as described elsewhere.[26]

3. RESULTS AND DISCUSSION

3.1. Catalytic performance for ethane ODH

Table 1 shows the catalytic performance during the ODH of ethane of the unpromoted and promoted catalysts. In the case of unpromoted (**Un-NiO**) and La-promoted (**La-NiO**) catalysts, the selectivity to ethylene was low. However, Nb- and

Sn-promoted NiO catalysts (i.e. **Nb-NiO** and **Sn-NiO** samples) present high selectivity to ethylene, which is in agreement with previous results on similar catalysts.[23]

Table 1

We must also inform that the catalytic performance observed for both **Nb-NiO** and **Sn-NiO** catalysts in the oxidative dehydrogenation (ODH) of ethane is very similar in terms of both the catalytic activity and the selectivity to ethylene. Thus, using typical reaction conditions for the ODH of ethane (Fig. 1), both catalysts presented an ethane conversion of ca. 9% with a selectivity to ethylene of ca. 84% (and ca. 16% to carbon oxides). It must be noted that in these conditions the carbon balance closed at 100±3% in all experiments conducted.

Figure 1

In order to check the robustness of both catalysts under reductive conditions, catalytic tests in the absence of oxygen in the feed ($C_2/O_2/He$ = 5/0/95 molar ratio) were carried out after 2 h on line. In the case of **Nb-NiO** catalyst, the ethane conversion increased from ca. 9% to ca. 22% when the oxygen was turned off and replaced by helium (Fig. 1a). At this point an increase in the carbon oxide selectivity (from ca. 17% to ca. 40%) was initially observed whereas the olefin was not detected anymore (Fig. 1b). However, methane was the main reaction product (with a selectivity of ca. 60%). Half an hour later, the ethane conversion decreased (due to the drastic decrease in the formation of carbon oxides) and the selectivity to methane increased until ca. 95%. After this point, the ethane conversion continuously grew whereas the selectivity to methane and carbon oxides kept stable at around 95 and 5%, respectively. It must be indicated that hydrogen was also observed in all the analyses without O_2 in the feed and that the carbon balance decreased until ca. 75 % once oxygen was replaced by helium.

This is due to the formation of large amounts coke on the catalyst as it was corroborated after reaction.

In the case of **Sn-NiO** catalyst, the catalytic behavior was surprisingly different (Fig. 1c and 1d). Thus, ethane conversion decreased from ca. 9% with oxygen in the feed to 0.5% when the oxygen was replaced by helium (Fig. 1c). On the other hand, an increase in the selectivity to ethylene from ca. 84% to ca. 93% was observed (with the corresponding decrease in the selectivity to carbon dioxide from ca. 16% to ca. 7% (Fig. 1d). Eventually, the conversion went on decreasing for the next 4 h on line.

According to these experiments the activation of ethane being similar in the presence of oxygen in the feed, follows different trends once the oxygen is absent. Apparently, nickel species in **Nb-NiO** catalyst undergo a relatively fast reduction to metallic nickel, which is highly active in the reforming of hydrocarbons (forming hydrogen and methane). In contrast, in the case of **Sn-NiO** catalyst, these species should remain in a relatively oxidized state in absence of oxygen in the feed, decreasing the ethane conversion below 0.5 %. The low amounts of ethylene and carbon oxides in the absence of oxygen in the feed are the result of the reaction of the ethane with the lattice oxygen species of the catalyst, following a MVK mechanism.

The reduction of Ni^{2+} species in **Sn-NiO** was only observed after several hours on-line and after increasing the contact time and the reaction temperature (Fig. S1). Accordingly, it seems that Ni^{2+} species in **Nb-NiO** catalyst should be remarkably more reducible in O_2-free ethane atmosphere than in **Sn-NiO** catalysts.

3.2. Characterization of fresh catalysts

Figure 2A shows XRD patterns of fresh catalysts, which present main Bragg signals at 2θ values corresponding to NiO cubic phase (Fm3m, ICSD No: 184626). All the promoted materials present significantly broader signals, which are related to a decrease in the crystallinity and the particle size of NiO. In fact, mean crystallite size was estimated using Scherrer equation, showing lower crystal size for **Nb-NiO**, **Sn-NiO** and **La-NiO** samples (8, 15 and 10 nm, respectively) with respect to pure **Un-NiO** sample (30 nm). However not significant differences were observed in cell parameters ($a \approx 4.17$ Å), which were calculated by XRD profile fitting (Table 1). In addition, diffraction signals related to the presence of additional crystalline phases as minorities, i.e. Nb_2O_5 (JCPDS: 01-071-0336), SnO_2 (JCPDS: 00-046-1088) or $La_2O_2CO_3$ (JCPDS: 00-048-1113), can be observed in the XRD patterns of **Nb-NiO**, **Sn-NiO** and **La-NiO** catalysts, respectively (Fig. 2A, patterns *a* to *c*). Interestingly, diffraction lines corresponding to SnO_2 appear much broader than those observed for Nb_2O_5 and $La_2O_2CO_3$, suggesting the presence of very small SnO_2 particles in **Sn-NiO** catalyst.

Figure 2

Bulk average composition of promoted catalysts, determined by EDX, indicates the presence of Nb and Sn contents of ca. 5.9 and 8.5 at. %, respectively (Table S1, Supporting information). However, EDX line-scans indicates the presence of with Nb atomic concentration of *ca.* 5-11 at. % in Nb-containing sample (Fig. 3A) and the presence of Sn atomic concentration of ca. 0.5-1.0 at. % in Sn-containing sample (Fig. 3B). Accordingly, the fact that the lattice parameter *a* of the **Nb-NiO** sample does not vary with respect to **Un-NiO** (Table 1) at these doping levels (ca. 5.9 %) could be explained by the presence of Nb_2O_5 as secondary phase and/or the presence of Nb^{5+} extra-framework species, likely on the catalyst surface. On the other hand, NiO particles in **Sn-NiO** sample present very low promoter concentration (*ca.* 0.5 % Sn as determined by EDX line-scans) (Fig. 3B and Fig. S4 B). This means that almost all the Sn must be forming SnO_2 in **Sn-NiO** catalyst.

Interestingly, both catalysts show a slight enrichment in surface promoter concentration (determined by XPS), with respect to their corresponding bulk composition (calculated by EDX) (Table S1). This could be explained in terms of SnO_2 distribution in **Sn-NiO** or, in the case of **Nb-NiO**, either by the presence of extra-framework Nb species and/or the formation of a Nb enriched surface Nb-Ni-O mixed phase (as reported by Millet et. al. [15]). In this sense, the different distribution of the promoter is in agreement with the features observed by Raman spectroscopy. Thus, NiO deformation modes [32] are shifted from 494 cm^{-1} in the unpromoted NiO catalyst to 527 cm^{-1} in Nb-promoted catalyst. This is likely due to a higher interaction of the promoter with NiO lattice (Figure S2). In the case of the Sn-promoted catalyst, we have not detected significant differences with the unpromoted sample. Hence, at least at the bulk level, Nb atoms significantly modify the original NiO framework; meanwhile Sn atoms must be just acting as surface promoters.

In fact, HAADF-STEM images and EDX maps (Figures S3 and S4) show a homogeneous distribution of Nb in **Nb-NiO**, whereas SnO_2 nanoparticles are mainly covering NiO in the case of **Sn-NiO** sample. This completely different promoter phase distribution and morphology shows that it is possible to attain similar interaction by an intimate contact between the nickel oxide and promoter (with the consequent modification of Ni active sites), as in the case of Sn-NiO, and achieve high selectivity to ethylene in the ODH of ethane.

Figure 3

To further understand the interaction of the promoters with NiO framework, fresh catalysts were also analyzed by XPS (Figure S5). On the one hand, Ni 2*p* core level shows an increase in the relative intensity of the satellite peak at 855.2 eV for promoted catalysts (Figure S5 A). This peak has been associated to the presence of several defects, like Ni^{2+}-OH [33], Ni^{2+} vacancies [34] or Ni^{3+} cations [35]. On the other hand, O 1*s* core level displays two main zones at 527.0-529.5 eV, assigned to O lattice species; and at 530.0-533.0 eV related to O species associated to defect sites like Ni^{2+} vacancies or Ni-OH, but also to oxygen atoms in organic species (Figure S5 B).[36] The relative intensity of the latter, ascribed to defects, increases in **Sn-NiO** and **Nb-NiO,** likely due to their lower particle size (Table 1).

Reducibility of unpromoted and promoted NiO catalysts was initially studied by means of H_2-TPR (Fig. 2B, Table 1). All the samples present two reduction peaks, although the temperature of the TPR peak maxima (the values of T_M) changes depending on the nature of the promoter: **Nb-NiO** (357 and 406ºC); **Sn-NiO** (300 and 331ºC); **La-NiO** (308 and 333ºC); and **Un-NiO** (298 and 321ºC). This can be related to the different step proposed for the reduction of NiO, i.e. NiO → $Ni^{\delta+}$ → Ni^0.[32] However, in the case of promoted and/or supported catalysts, other reduction peaks were observed, including NiO with high interaction with the support.[33] In this way, a small peak (as minority) is also observed at ca. 291ºC, which could be related to the presence of some unpromoted NiO particles. Overall, the temperature for the maximum in the TPR profiles decreases in the following trend: **Nb-NiO** > **Sn-NiO** > **La-NiO** > **Un-NiO.**

The appearance of these peaks at higher temperatures can be ascribed to Ni species presenting different reducibility.[34] It has been proposed that nonstoichiometric NiO shows the lower initial activation energy of reduction, whereas stoichiometric NiO shows a higher initial activation energy for starting the autocatalytic nucleation.[34] In this regard, the intensity of the low temperature reduction peak decreases when Nb or Sn were used as promoters. Accordingly, an increment of the relative intensity of the signal appearing at higher reduction temperatures was also observed for these samples (i.e. for peaks appearing at 357 and 331 ºC, for **Nb-NiO** and **Sn-NiO**). These facts suggest that high reducible Ni species could partially be transformed when adding Sn^{4+} and Nb^{5+} as promoters (and, to a lower extent, for La-containing sample), which would lead to higher ethylene yield in ODH of ethane.

3.3. In-situ XAS study

In-situ time-resolved Ni K-edge XANES measurements were performed during reduction-reoxidation-reduction sequential treatments under H_2/He, O_2/He and C_2H_6/He mixtures respectively. All the samples present transitions between typical XANES features of a pure NiO, showing high intensity white line at 8349 eV and a very low intensity shoulder at *ca*. 8334 eV, and those typical features of metallic Ni, displaying a broad shoulder at 8334 eV and a very low intensity white line at 8349 eV.[35]

Figures 4 and 5 depict both in-situ time-resolved normalized Ni K-edge XANES spectra recorded at 450ºC (Fig. 4), and their corresponding kinetic curves obtained by linear combination fitting (Fig. 5), of unpromoted and promoted NiO catalysts (see also Figure S6 and Table S2). It can be seen that these catalysts present different behavior under reduction/reoxidation/reduction cycles, especially when comparing Nb- and Sn-promoted catalysts. In addition, important differences are also observed for unpromoted and La-promoted catalysts.

Figure 4

Figure 5

Nb- and Sn-promoted catalysts (Fig. 4a and 4b, respectively) present similar slow reduction rate under H_2/He atmosphere (step 1). However, **Nb-NiO** catalyst suffers an instantaneous total reoxidation under O_2/He (step 2), meanwhile **Sn-NiO** shows a progressive partial reoxidation (until 79 % NiO) under the same conditions. In addition, they also show significant differences under C_2H_6/He reduction. Thus, after a short induction period, **Nb-NiO** rapidly reduces almost 100 % (step 3), while **Sn-NiO** is not reduced after *ca.* 30 min (which is in good agreement with the catalytic results under C_2H_6/He reduction (Figure 1c) (Figure S1). It is noteworthy to mention that the fact of not reaching total reoxidation in **Sn-NiO** catalyst could affect the subsequent reduction treatment under C_2H_6/He.

According to these results, the presence of metallic Ni on the catalyst could promote ethane reforming reactions (when the experiments are carried out in the absence of oxygen), causing the formation of carbon deposits on the surface, hindering NiO reduction. Despite this, morphology and microstructure of **Sn-NiO** material can play a significant role, as it will be discussed later.

In the case of **La-NiO** and **Un-NiO** catalysts, the least selective catalysts for ethane ODH, both materials show faster H_2 reduction kinetics (**La-NiO** > Un-**NiO**) than that observed for **Nb-NiO** and **Sn-NiO** (see also in Figure S6 and Table S2). However, **La-NiO** undergoes a very fast total reoxidation (≈ 100% NiO) under O_2/He atmosphere (step 2); meanwhile **Un-NiO** catalyst undergoes a progressive incomplete reoxidation (70 % NiO). In this regard, the relatively better performance of **La-NiO** with respect to **Un-NiO** in the ODH of ethane could be explained by means of its higher reoxidation capacity, which would help to keep Ni in +2 oxidation state during catalytic cycles. Finally, reduction under C_2H_6/He shows slower reduction rate for **Un-NiO** (step 3), which could be explained either by the formation of carbon deposits by catalytic reforming of ethane on the remaining metallic Ni sites (as a result of an incomplete previous reoxidation under O_2/He), or by the presence of larger NiO particles.

These results suggest that both reduction and to a lesser extent the oxidation stages during the catalytic cycle play an important role on the catalytic performance in the

ODH of ethane. Thus slow reduction (and preferably fast reoxidation kinetics) would help to keep a more controlable oxygen supply during the catalytic cycles in the ODH of ethane, favoring ethylene formation and decreasing the selectivity to CO_x. However, results obtained in the reduction experiments with C_2H_6/He suggest that other variables, such as particle size, phase distribution of the promoter, or the formation of carbon deposits could have some influence on the catalytic behavior of these materials when oxygen is not present.

In order to clarify these aspects, in-situ Ni K-edge measurements were carried out during reduction and re-oxidation of **Un-NiO** and **Sn-NiO** at 500 ºC under reaction conditions (without and with oxygen in the feed) (Figure S7). **Ni-SnO** sample shows the same behavior previously described, i.e. it remains oxidized after *ca.* 1 h under reductive atmosphere (Figure S7, c and d). Thus, under these conditions, no reforming of ethane can occur as no metallic Ni is present in the fresh catalyst, and big amounts of coke cannot be formed. Therefore, its resistance to reduction by ethane must be mainly due to intrinsic features of the material. Regarding **Un-NiO**, it also presents a similar induction period during reduction, and it does not achieve total reoxidation when oxygen is introduced in the feed (Figure S7, *a* and *b*), likely because of its higher particle size. Hence, these results permit us to ascribe the behavior in both re-oxidation and the reduction under ethane principally to aspects related to morphology, microstructural features and/or particle size of the oxides, although the formation of some carbon species cannot be totally ruled out.

The Ni K-edge spectra and the corresponding kinetic curves for **Nb-NiO** and **Sn-NiO** obtained by LCF at 400, 450 and 500ºC are shown in Figures 6 and 7, respectively. In all cases, the experiments were conducted during reduction-reoxidation-reduction sequential treatments (under H_2/He, air and C_2H_6/He, respectively). **Nb-NiO** displays instantaneous re-oxidation regardless of the temperature. However, it has a significant effect on the reduction kinetics, being faster as the temperature increases, under both H_2/He and C_2H_6/He atmospheres (Fig. 6) (Table S3). On the other hand, The Ni K-edge spectra and the corresponding kinetic curves of **Sn-NiO** catalyst present differences under both reductive and oxidative conditions (Fig. 7) (Table S4). Under H_2/He (step 1), a decrease in the time of reduction occurs as the temperature increases, meanwhile reduction conducted under C_2H_6/He does not take place in the time range examined, regardless of the reaction temperature. Under O_2/He (step 2), **Sn-NiO** undergoes progressive reoxidation, achieving different reoxidation degree depending on the temperature.

Figure 6

Figure 7

Figure 8 presents XANES features of **Sn-NiO** sample treated under O_2/He after 12 min of reoxidation treatment at 400, 450 and 500ºC. It can be observed that as the temperature increases, reoxidation degree achieved decreases. The aggregation of SnO_2 particles surrounding NiO particles (which would hinder catalyst reoxidation) can explain this anomalous behavior.

Figure 8

3.4. Characterization of used Sn-NiO and Nb-NiO catalysts

As indicated previously, the XRD patterns of fresh **Nb-NiO** and **Sn-NiO** catalysts are characterized by the presence of NiO, and particles of Nb_2O_5 or SnO_2, respectively (Fig. 2A, patterns a and b, and Fig. 3). In addition, important differences have been observed when comparing the same samples after treatment in a C_2H_6/He mixture at 450ºC. In the case of **Nb-NiO** sample (Fig. 9A), NiO and Nb_2O_5 phases are reduced into fcc metallic Ni (JCPDS: 01-070-1849) and NbO_2 (JCPDS: 01-0.74-2387) respectively. However, **Sn-NiO** remains unreduced, presenting the same diffraction signals observed in the case of the fresh catalyst, corresponding to NiO (JCPDS: 78-643) and SnO_2 (JCPDS: 00-046-1088) phases (Fig. 9B). These results are in good agreement with in-situ XANES experiments suggesting that, in some manner, the presence of SnO_2 crystals in Sn-NiO sample protect and/or inhibit the reduction of NiO particles.

Figure 9

EDX maps conducted on **Nb-NiO** and **Sn-NiO** samples treated at 450ºC in the absence of oxygen are shown in Figure 9 (pictures C and D, respectively). A uniform distribution of carbon over the surface of unreduced NiO and SnO_2 on **Sn-NiO** catalyst can be observed (Fig. 9 C), meanwhile **Nb-NiO** presents wire-shaped carbon particles, probably due to its relatively fast reduction process (Fig. 9 D). Hence, this suggests that although no metallic Ni is present in the fresh catalyst, some carbon is also formed on its surface when oxygen is not present in the feed, which could also help to prevent the reduction by ethane.

Interestingly, stability experiments performed on **Sn-NiO** at higher temperature and contact time in the absence of oxygen (Figure S1) gave rise to the formation of metastable metallic hcp-Ni phase (JCPDS: 45-1027) (Fig. S8 A), which has been reported to be obtained just in special conditions, as in the case of NiO being protected by the presence of graphite.[36] Indeed, EDX maps performed on reduced **Sn-NiO** show a thick layer of carbon deposits covering the reduced catalyst (Figure S8, images B and C). Additionally, XPS analyses of reduced catalysts show a higher concentration of carbon on the surface of Sn-NiO catalyst (Table S5).

3.5. General remarks

The redox properties of Nb- and Sn- promoted NiO catalysts, both presenting high selectivity during the ODH of ethane to ethylene, have been studied. These samples are characterized by the presence of NiO with small crystal size, although it depends on the nature of the promoter. For a better comparison the redox properties of La-promoted (with a similar crystal size than those observed in Nb- and Sn-promoted NiO) and unpromoted NiO, which show a relatively low selectivity to ethylene during the ODH of ethane, have also been studied.

The catalytic behavior of these catalysts is related to the reducibility of Ni^{2+} species, in a way that the best catalysts are those presenting the slowest reduction rate, whereas materials presenting faster reduction kinetic show the lowest selectivity to ethylene. In addition, the catalyst reoxidation seems to play also a role on the catalytic performance, since a fast reoxidation rate improves ethylene formation when comparing unpromoted and La-promoted NiO catalyst. However, this reoxidation rate seems to be dependant on the distribution of the promoter and the NiO particle size, as it has been shown for Sn-promoted and unpromoted NiO materials.

Despite Nb- and Sn-promoted NiO present similar catalytic performance in the ODH of ethane in presence of oxygen, they show very different promoter distribution and catalytic performance in the absence of O_2 in the feed. In this way, the aggregation of SnO_2 particles surrounding NiO particles (which would hinder catalyst reoxidation) can explain the extremely low reducibility under ethane atmosphere in the absence of O_2 of Sn-promoted NiO catalyst. This fact indicates that it is possible to achieve the proper interaction between the promoter and the NiO without introducing the doping metal into nickel oxide framework (i.e. by intimate contact with a promoter oxide on the surface), achieving similar high selectivity in the ODH of ethane. Accordingly, the way of interaction of Sn and Nb is substantially different, as it was shown by XPS and Raman spectroscopy and electron microscopy.

Unlike the ODH of ethane, the promoter distribution in these catalysts affects the catalytic performance in the absence of oxygen. Thus, a uniform distribution of carbon over the surface of unreduced NiO and SnO_2 on **Sn-NiO** catalyst was observed (which can also help to prevent reduction by ethane), meanwhile **Nb-NiO** presents wire-shaped carbon particles (probably due to its faster reduction rate caused by its different phase distribution).

4. CONCLUSIONS

The relationship between the redox properties and the catalytic performance of unpromoted and promoted (Nb-, Sn- or La-) NiO catalysts in the oxidative and non-oxidative activation of ethane has been studied. In this way, Nb-NiO and Sn-NiO catalysts are highly efficient in the ODH of ethane, showing an extremely similar performance. The reducibility of Ni^{2+} species seems to play an important role, being more selective those catalysts presenting a lower reduction rate. The reoxidation rate also seems to influence the catalytic performance although, in our experimental conditions, to a lesser extent.

However, the behavior of these catalysts in absence of oxygen (ethane/helium mixture) is completely different. Thus, Ni^{2+} is completely reduced to Ni^{o} in the Nb-containing catalyst, leading to the formation of methane, coke and hydrogen. However, more extreme conditions are needed to partially reduce Sn-NiO catalyst. According to electron microscopy results, the coverage of NiO particles by small SnO_2 particles hinders the Ni^{2+} reduction to Ni^{o}, fact that is not observed in the case of the Nb-NiO catalyst (due to the high Nb-distribution on NiO). In addition, a uniform distribution of carbon (confirmed by both electron microscopy and XPS of used catalysts) tends to cover the surface of unreduced NiO and SnO_2 on **Sn-NiO** catalyst, likely obstructing the reduction by ethane. However, abundant wire-shaped carbon particles are observed on **Nb-NiO** catalyst, probably as a consequence of the faster reduction rate.

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Supporting Information. The following information is available free of charge on the ACS Publications website at doi:_ : Catalytic results of Sn-promoted NiO at more severe conditions, table showing bulk and surface compositions of fresh Sn- and Nb-promoted materials, Raman spectra of Sn- and Nb-promoted NiO, and unpromoted NiO, HAADF-STEM images and EDX analysis of fresh catalysts (Sn- and Nb-promoted NiO), summarized fitted and experimental Ni K-edge XANES spectra, in-situ Ni K-edge XANES spectrum and their corresponding LCF-kinetics under reaction conditions of Sn-promoted and unpromoted NiO (without and with oxygen); XRD, BF- STEM image and EDX map of reduced Sn-promoted NiO, tables summarizing the LCF results obtained at different temperatures for Sn- and Nb-promoted NiO under H_2/He, O_2/He and ethane/He atmosphere and surface composition of reduced Sn- and Nb- promoted catalysts.

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Notes

The authors declare no competing financial interests.

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Table 1. Physico-chemical and catalytic properties of unpromoted and promoted NiO.

sample	particle size (nm) [a]	cubic cell parameter (Å)	H_2-TPR T_M (ºC) [b]	ethane conversion (%)[c]	selectivity to ethylene (%)[c]
Nb-NiO	8	4.1759	357	8.6	83.4
Sn-NiO	15	4.1767	331	8.8	83.7
La-NiO	10	4.1714	308	8.4[d]	52.4[d]
Un-NiO	30	4.1760	298	7.0	37.1

a) Calculated using Scherrer equation.

b) T_M, temperature for maximum H_2-uptake during H_2-TPR experiments. In these experiments, the H_2-uptakes for **Nb-NiO**, **Sn-NiO**, **La-NiO**, and **Un-NiO** catalysts were: 19.57, 21.54, 22.59 and 20.61 $mmol_{H2}\ g_{Ni}^{-1}$, respectively.

c) Experimental conditions: $C_2/O_2/He$ molar ratio of 5/5/90; reaction temperature: 450ºC; contact time, W/F, of 2 g_{cat} h $(mol_{C2H6})^{-1}$.

d) Contact time, W/F, of 1 g_{cat} h $(mol_{C2H6})^{-1}$.