

# Low temperature CO oxidation and ethane oxidative dehydrogenation over Nb-doped nickel oxides

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## Introduction

Oxidative dehydrogenation (ODH) of ethane is a reaction of industrial importance, which allows production of ethene under mild conditions. Despite high activation energy for oxygen desorption from NiO [1], Ni-based catalysts unexpectedly turned out to be good candidates for low temperature ethane ODH [2]. Their selectivity could be improved by doping the crystal structure with 15at.% of niobium [3]. Mechanistic studies have suggested that, by filling the cationic vacancies, niobium reduces the number of active sites for oxygen dissociation. This enhances diffusion of unselective, “electrophilic” O<sup>-</sup> oxygen species inside the bulk and increasing the number of less labile, selective, “nucleophilic” O<sup>2-</sup> oxygen species on the surface [4]. Here, we report the effect of niobium doping of NiO, in the 0-22 at.% range, for the catalytic oxidation of CO both in the presence and in the absence of hydrogen. This behavior correlates with that observed in low temperature ethane ODH and we bring structural evidence for the impact of niobium doping on the number of oxygen vacancies.

## Experimental

NiO was prepared by a sol-gel method [5]. Ni<sub>x</sub>Nb<sub>1-x</sub>O (x = 0.95, 0.9, 0.85, 0.78) were prepared by modifying the protocol as follows for the e.g. Ni<sub>0.85</sub>Nb<sub>0.15</sub>O composition. 0.46 g NbCl<sub>5</sub> is slowly added to 30 ml H<sub>2</sub>O. The resulting white Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O precipitate is washed with H<sub>2</sub>O until free of chlorine. It is then dissolved in warm citric acid solution (50 mL, 0.21 mol L<sup>-1</sup>). When 3 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O are added, the initially transparent solution turns blue. It is then kept at 80°C under stirring for 12 h. The resulting gel is dried at 120°C for 12 h and calcined at 450°C for 4 h. The Ni-Nb mixed oxides are characterized by N<sub>2</sub> physisorption, SEM, TEM, XPS and XRD. Rietveld analysis was performed by using the Highscore Plus Software from PANalytical. Their catalytic properties are evaluated at atmospheric pressure in the oxidative dehydrogenation of ethane and in the oxidation of CO using a P&ID micro-pilot (i.d. 10 mm) and a high-throughput Flowrence reactor from Avantium (i.d. 2 mm), gas mixtures of 10% C<sub>2</sub>H<sub>6</sub> / 5% O<sub>2</sub> in He and 1% CO / 1% O<sub>2</sub> / 0% or 37% H<sub>2</sub> in N<sub>2</sub>/He, total flow rates of 10 mL/min and 12 mL/min, 100 mg (+ 300 mg SiC diluents) and 2.5 mg (+ 47.5 mg Al<sub>2</sub>O<sub>3</sub>

diluent) of catalyst ramped at 1°/min from 200 to 400°C and 40 to 280°C, respectively, and a Varian 490 micro-GC equipped with 2 MS5A, 1 PPQ and 1 PE columns.

## Results/Discussion

The surface areas of the nickel-based oxides are only slightly affected by Nb doping and the ethene production rates /weight from ethane are improved at low temperature by a Nb doping level of about 10-15at.%, in agreement with previous work [2, 3].

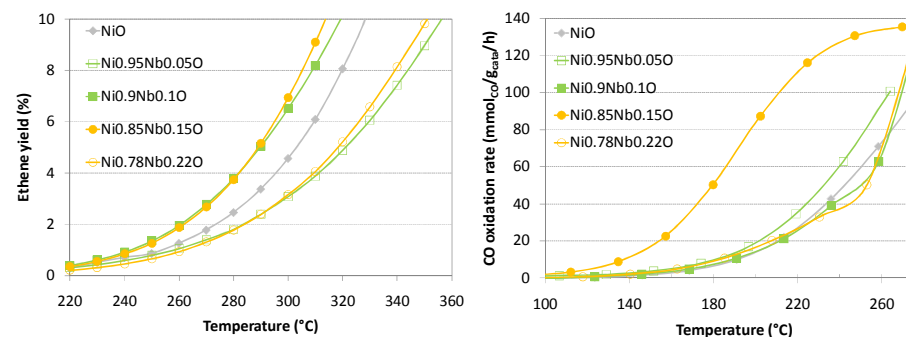


Figure 1. Ethene yields and CO conversion obtained during oxidative dehydrogenation of ethane and CO oxidation (1% CO / 1% O<sub>2</sub> in N<sub>2</sub>/He) respectively, over Nb-doped NiO catalysts.

Interestingly Ni<sub>0.85</sub>Nb<sub>0.15</sub>O exhibits superior efficiency for low temperature CO oxidation as well (Figure 1), the other levels of doping leading to an activity similar to that of NiO. In the presence of hydrogen on the other hand, the lowest level of Nb doping (5 at.%) dramatically improves the total oxidation activity of NiO (the temperature of half oxygen conversion decreases from T<sub>1/2</sub> = 198°C to T<sub>1/2</sub> = 154°C). Increasing the level of Nb (10, 15 and 22 at.%) doping is detrimental to the catalytic activity, with T<sub>1/2</sub> reaching 177, 233 and 310°C, respectively, but it is favorable to the selectivity to CO<sub>2</sub> at iso-conversion. The role of oxygen vacancies in the processes will be highlighted on the basis of Rietveld analysis of the crystal structures.

## References.

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