



**UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
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DOCTORAL THESIS SUMMARY

NiO-BASED CATALYSTS FOR ETHANE OXYDEHYDROGENATION

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NiO-based catalysts for ethane oxydehydrogenation

This PhD focuses on the development of highly active and selective NiO-based catalysts for the oxidative dehydrogenation (ODH) of ethane to ethylene, a reaction of great industrial interest and a promising alternative to the conventional steam cracking process. Steam cracking, the predominant ethylene production method at present, is very energy-intensive, requires operating temperatures above 750 °C and generates significant CO₂-based emissions - up to 2 tonnes for every ton of ethylene produced. As global demand for ethylene continues to increase and production exceeds 177 million tonnes per year, there is an urgent need for cleaner and more energy efficient technologies that can deliver high ethylene yields while reducing the environmental impact. Oxidative dehydrogenation is a more sustainable route, offering the potential to operate at much lower temperatures and to reduce the energy consumption caused by endothermic cracking reactions. Moreover, by properly tailoring the properties of the catalyst, ODH can achieve high selectivity of ethylene while minimizing unwanted by-products such as CO₂ and coke. Among the different catalytic systems tested for this purpose, NiO-based materials showed a high potential for their intrinsic C-H bond activation, abundance, low toxicity in comparison to other oxide-based catalysts and ease of modification by the addition of dopants. The catalytic capacity of NiO can be adjusted by changing its surface oxygen distribution, crystallite size, acidity/basicity and reducibility, allowing selective oxidation of ethane to ethylene rather than total oxidation to CO₂. However, the key challenge is to establish clear structural, activity and selectivity relationships to guide the rational design of catalysts combining high activity, high selectivity and long-term stability under reaction conditions.

The thesis is divided into four main chapters:

Chapter 1 provides an extensive review of ethylene production technologies and outlines the advantages and limitations of ODH of ethane. The catalytic role of NiO is discussed in depth, including the influence of oxygen species type, the effect of non-stoichiometry, and the potential of doping to modulate surface chemistry. Literature data on various promoters (Ce, Sn, Al, Ta, Nb, Fe, P, Ti, W, Zr, Mo, V, Li, Mg, Ga, K) are analyzed, showing general trends: high-valence, acidic dopants (Nb⁵⁺, Ta⁵⁺, Sn⁴⁺, W⁶⁺) suppress electrophilic oxygen and improve ethylene selectivity, whereas low-valence dopants (Li⁺, Mg²⁺) tend to promote total oxidation. Among the first, the Nb-doped NiO with a Nb/Ni atomic ratio of 0.176 was found to be the best NiO-based catalyst for

ethane ODH. Key performance metrics from previous studies are summarized to highlight knowledge gaps addressed in this work.

Chapter 2 describes the experimental procedures for catalyst synthesis, characterization methods, and testing. NiO-based catalysts were prepared by 2 main routes – a method involving the low-temperature solvent evaporation, and hydrothermal synthesis under controlled pH and temperature – to achieve controlled dopant dispersion and surface chemistry. Comprehensive characterization was performed using X-ray diffraction (XRD), N₂ physisorption (BET), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), H₂ temperature-programmed reduction (H₂-TPR), scanning electron microscopy (SEM) together with X-ray energy dispersion analysis (EDX), and in situ electrical conductivity measurements. Catalytic performance was evaluated in a fixed-bed quartz tube reactor under atmospheric pressure, with ethane/oxygen molar ratio of 1 at temperatures between 325 and 425 °C, monitoring conversion, selectivity, and stability. The reaction products were analyzed by gas chromatography.

Chapter 3 presents a systematic study on the effect of Mg, Al, Mn, and Fe doping on the structural, surface, and catalytic properties of NiNbO mixed oxides in ethane ODH. All catalysts were prepared by the solvent evaporation route with a constant Nb/Ni ratio of 0.176 and (Ni+Nb)/M = 9 for doped systems. XRD analysis showed only the NiO phase, suggesting that Nb and dopants were incorporated into the lattice or highly dispersed. BET measurements indicated that Mg- and Mn-doped samples had the highest surface areas, while XPS revealed dopant-induced changes in Ni and Nb surface states. SEM-EDX confirmed uniform elemental dispersion in all samples. Cation M modifiers markedly influenced the redox, semiconductive, and catalytic properties of NiNbO in ethane ODH. M-free NiNbO delivered the best balance of activity and selectivity, while Mn- and Fe-modified catalysts favored either higher low-temperature activity or greater ethylene selectivity, respectively. Al-NiNbO showed the slowest deactivation, yet no catalyst was fully stable at 400 °C. Deactivation correlated with a decline in p-type conductivity and redox capacity under reaction conditions. Overall, the study established that dopant type can tune the balance between activity and selectivity by modifying oxygen species availability and oxide reducibility.

Chapter 4 examines the effect of high-valency dopants Sn, Ti, Sb and Ta on NiNbO catalysts, focusing on the stability and performance of systems containing Ta in ethane ODH. All catalysts have been synthesized by hydrothermal synthesis, except for Ti-NiNbO which was prepared by solvent evaporation. The Ta-containing catalyst was also prepared at pH 8 with the compositions

(NiNb)_{0.9}Ta_{0.1}O and (NiNb)_{0.95}Ta_{0.05}O, labeled Ta-NiNbO-8 and Ta(5)-NiNbO-8, respectively. XRD showed that while the Sb, Ti and Ta-modified samples showed only NiO reflections, the catalyst modified with Sn also contained crystalline SnO₂. The Ta-modified systems prepared at pH 8 showed additional unidentified diffraction lines. XPS revealed that M doping shifted the Ni²⁺ peak to higher binding energies, with Ta-containing catalysts showing the largest shift and a Ni³⁺-dominated surface, likely due to interaction with Nb⁵⁺ species. Electrical conductivity measurements under different atmospheres showed that Ta-containing catalysts exhibited the largest reduction extent under reaction conditions, indicating a lower density of these active but less selective O⁻ sites, which explains their enhanced catalytic selectivity. Catalytic tests showed that Ta(5)-NiNbO-8 gave the best results, maintaining a relatively stable ethane conversion and ODH selectivity up to 20 hours in flow and then slowly deactivating. This is attributed to the reduction in the active site density due to Nb surface enrichment, the decrease in the Ni³⁺/Ni²⁺ surface ratio and the growth of NiO crystals, together with the reduction in the redox capacity of the catalyst. Although incorporation of Ta improved stability compared to undoped NiNbO, recovery after deactivation was not possible.

The general conclusions are detailed at the end of the doctoral thesis.