

Understanding NiO-MeO_x interactions in promoted and supported NiO-based catalysts for the ODH of ethane

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Abstract: Promoted and supported NiO catalysts can be extremely selective in the oxidative dehydrogenation of ethane (ODH) to ethylene. However, the composition of the catalysts has to be controlled in order to achieve the optimal catalytic performance, which depends on the synthesis method. This study includes Ni-Ti-O, Ni-Nb-O and Ni-Sn-O systems.

Keywords: Promoted and supported NiO catalysts, ODH of ethane, Ethylene.

1. Introduction

Ethylene is the most important building block in petrochemistry.¹ However, at the moment, it is mainly obtained by steam cracking.^{1,2} An alternative could be the ethane oxidative dehydrogenation, a low energy-demanding process, although the selectivity must be improved.³ Among the different catalytic systems proposed, NiO-based catalysts are one of the more selective ones,⁴ especially those promoted with Nb or Sn oxides⁵ or supported on TiO₂-based materials.⁶ In this paper we show a comparative study about both promoted and supported NiO catalysts (using TiO₂, Nb₂O₅ or SnO₂ as promoters or as supports) in order to understand the key aspects to achieve high selectivity to ethylene during the ODH of ethane.

2. Experimental

Series of MeO_x-promoted and MeO_x-supported NiO catalysts (with different NiO contents, Me: Ti, Nb and Sn) have been prepared by wet impregnation and co-precipitation, respectively, according to procedures previously reported.^{5,6} All the catalysts were activated at 500 °C for 2 h. The materials were characterized by XRD, N₂ adsorption, TEM, FTIR of adsorbed CO, XPS, and X-ray Absorption Spectroscopy. The catalytic tests were carried out in a fixed bed reactor. The analysis of reactants and products was performed by gas chromatography.⁶

3. Results and discussion

Initially, two Ni-Ti-O catalysts with 20 wt% NiO were synthesized by: i) precipitation of aqueous solution of Ti- and Ni-salts (promoted catalyst); and ii) by wet impregnation of TiO₂ with an aqueous solution of Ni-salt (supported catalyst). In spite of the fact that the final composition of the catalysts was almost identical, the catalytic results obtained during the oxidative dehydrogenation were very different. The catalytic activity was higher in the supported catalyst than in the promoted one (*ca.* 30% higher). In addition, if the selectivity to ethylene is plotted with the ethane conversion at a fixed temperature, the supported catalyst presents a quite flat profile. The selectivity to ethylene hardly decreases when increasing the ethane conversion (until *ca.* 20%), and reaches *ca.* 90% in the whole range of conversions studied. In the case of promoted catalyst, the selectivity to ethylene was high (> 90%) at low conversions. However, important ethylene decomposition was observed when increasing ethane conversion ($S_{\text{ethylene}} < 70\%$ at 15% of ethane conversion).

A detailed characterization of these catalysts was conducted in order to elucidate the main causes of their different catalytic behavior. H₂-TPR indicates that the supported sample presents higher reducibility. Thus, the maximum H₂-uptake for the supported catalyst appears at 298°C, whereas it appears at 382°C in the case of the promoted material (Table 1). This fact could be related to the lower catalytic activity of the promoted catalyst. XPS studies reveals that the surface characteristics are very different. Although the nature of the Ni-species was similar between both samples, the proportion of O-species remarkably varies. For both

catalysts surface nickel was present predominantly as Ni²⁺, showing a very similar profile. However, the O α /O β ratio is much higher in the supported material. Moreover, although the overall bulk composition is very similar, the supported catalysts presents a higher proportion of surface Ni. Indeed, Ni/Ti surface ratio for the supported catalyst was 0.85, being Ni/Ti = 0.46 in the case of promoted sample. In fact, the higher amount of free surface Ti-sites in the promoted catalyst could facilitate the ethylene decomposition into carbon dioxide, since TiO₂ tends to completely oxidize hydrocarbons at the temperatures range studied in this work.

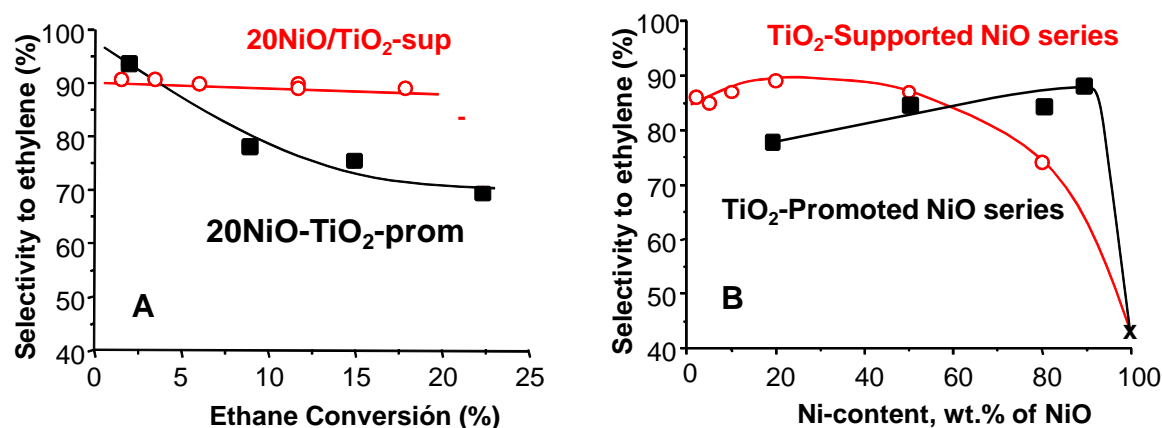


Figure 1. Catalytic performance of supported and promoted Ni-Ti-O catalysts. A) Variation of the selectivity to ethylene with the propane conversion and B) Influence of the NiO-loading on the selectivity to ethylene (isoconversion of 10%). Reaction conditions: 450°C and ethane/O₂/He = 3/1/26 (molar ratio)

Table 1. Physicochemical characteristics of promoted and supported Ni-Ti-O catalysts.

Sample	S _{BET} (m ² g ⁻¹)	TPR		Ni/Ti at. ratio		XPS results		
		T _{Max} (°C)	H ₂ -uptake	Bulk	XPS	S(I)/Main	S(II)/Main	O α /O β
20Ni-sup	50.4	298	3.65	0.21	0.85	1.58	1.99	16
20Ni-prom	58.9	382	4.06	0.22	0.46	1.46	1.96	2.4

We have also extended the study to other NiO-loadings (Fig. 1B). Interestingly, both preparation methods led to different trends. Supported catalysts present an optimum performance for a NiO-loading of 20-40%. However, promoted samples with ca. 90 wt% NiO display the highest selectivity to ethylene. The different Ni-Ti interaction as well as the amount of free titania sites can be the origin of the different behavior. XPS and EXAFS analysis suggest that outstanding catalytic performance in the ODH of ethane (i.e. high selectivity to ethylene) must be related to the presence of Ni and O vacancies.

A similar study has been undertaken with Ni-Nb-O and Ni-Sn-O catalysts, studying the differences between supported and promoted materials and the role of the second metal oxide.

4. Conclusions

Ni-Ti-O, Ni-Nb-O and Ni-Sn-O catalysts are highly efficient in the oxidative dehydrogenation of ethane. However, the catalytic performance strongly depends on both the preparation method and the composition of the catalysts. Factors such as the NiO reducibility, the interaction between nickel oxide and the second element (Ti, Nb or Sn) and the amount of free unselective sites determine the catalytic behavior.

References

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