



Comparison of Ni and Ni–Ce/Al₂O₃ catalysts in granulated and structured forms: Their possible use in the oxidative dehydrogenation of ethane reaction

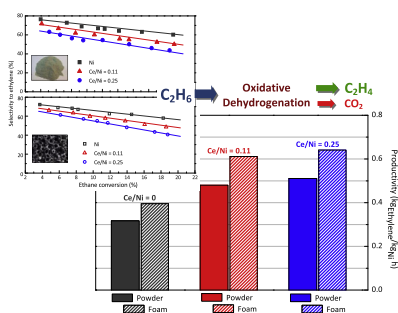
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HIGHLIGHTS

- Ni and Ni–Ce/Al₂O₃ coatings on metallic foams were active and selective for the ODE.
- The cerium addition increased considerably the ethylene productivity.
- Catalytic features of the structured systems depend on the calcination temperature.
- The presence of chromium in the catalytic coatings mainly affects the selectivity.
- The structured systems showed higher ethylene productivity than powder catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

Ni and Ni–Ce/Alumina catalysts in structured form were prepared, characterized by different techniques and tested in the oxidative dehydrogenation of ethane (ODE). In order to gain further insight into active species, catalysts in granulated form were also synthesized, characterized and evaluated in the same reaction test.

The results indicated that the Ni and Ni–Ce/Al₂O₃ granulated catalysts were active and selective for this reaction. The addition of cerium using two atomic ratios (Ce/Ni = 0.11 and 0.25) significantly increased the ethylene productivity by kg of nickel mainly motivated by the marked increment in ethane conversion. This behavior could be explained by the smaller nickel oxide crystallite size and the incorporation of nickel into the ceria lattice.

The structured systems showed similar active species but achieved a better performance in terms of ethane conversion and ethylene productivity, compared with the granulated forms. The higher catalytic activity could be associated with the presence of lower crystallite sizes of the active phases and also related to a better utilization of active sites due to a higher accessibility of the reagents to the catalyst surface.

The existence of certain species (mainly chromium oxide) in the coverage also contributed to obtain higher conversion even though the selectivity to ethylene decreased. Lower temperature treatments applied to the structured support (550 °C instead of 700 °C) reduced the amount of these undesired species that favor the total oxidation of ethane.

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1. Introduction

Ethylene is an important building block in the petrochemical industry. Today, it is mostly produced by naphtha or ethane cracking [1]. This process employs severe operating conditions and shows a number of disadvantages such as thermodynamical limitations and coke formation.

Among the alternative routes to produce ethylene, the oxidative dehydrogenation of ethane emerges as an attractive reaction because it presents several advantages, i.e. lower operating temperatures and the presence of oxygen to produce water as co-product, thus allowing overcoming thermodynamical limitations.

Numerous catalytic powder formulations were investigated for the oxidative dehydrogenation of ethane (ODE) in which vanadium was a traditional choice as active component [2]. However, in the last few years, nickel-based materials have become promising catalysts due to their capability to activate light paraffins at relatively low temperatures [3–5].

On the other hand, ceria presents particular chemical features such as its redox properties in the presence of transition metals [6–9] which makes it very attractive for applications in catalytic formulations in numerous reactions. The main role played by ceria is related to the generation of anionic vacancies and to the participation of reactive oxygen species, which can be tuned in the presence of other elements in the lattice [10,11]. The Ni–Ce combination has been studied for many reactions, e.g. the reduction of nitrogen oxides [12], reforming [13,14], partial oxidation [15,16] and redox reactions [17–19], among others.

The employment of a catalytic formulation in granulated form is difficult if a practical or industrial application is considered; therefore, it is important to take into account the feasibility of depositing them onto a substrate which constitutes a structured catalyst. These systems could provide numerous advantages inherent to their nature and morphological characteristics, although there are still unresolved issues that prevent their use in certain production processes.

Very few reports have been published in the literature on structured systems applied to the oxidative dehydrogenation reaction at low temperatures and most of them are mainly devoted to propane [20,21]. Therefore, the development of non-conventional reactor configurations leading to an increasing energy efficiency and the optimization of the reaction temperature control as well as to higher values of activity and/or selectivity looks like an interesting challenge.

Among the many options from which to choose substrates, metallic foams present remarkable features, i.e. the simplicity of building different structures and better heat transfer coefficients than those of the ceramic monoliths, which are useful for exothermal reactions [22]. In addition, the flow regime is turbulent allowing a better mixing of reagents and increasing axial and radial dispersion [23].

In this context, the aim of this work was the preparation, physicochemical characterization and catalytic evaluation of structured catalysts in the oxidative dehydrogenation of ethane reaction (ODE). The systems were prepared using AISI 314 stainless steel foams as substrates for Ni and Ni–Ce/Al₂O₃ catalysts. In order to gain further insight into active sites, catalysts in granulated form were also prepared, characterized by several techniques and evaluated in the same reaction test.

2. Material and methods

2.1. Granulated catalysts

Monometallic (Ni and Ce) and bimetallic (Ni–Ce) oxide catalysts were prepared by wet impregnation and co-impregnation,

respectively, with a 15 wt% maximum loading. Alumina PURALOX Condea SBA-230 was used as support. Aqueous solutions of either nickel or nickel–cerium nitrates were used as metal precursors. In the mixture of these precursors, two different atomic ratios were used: Ce/Ni = 0.11 and 0.25. The solvent was removed by evaporation. The resulting granulated was oven dried for 8 h at 120 °C. Finally, it was calcined in air flow at 550 °C for 4 h.

2.2. Structured catalysts

AISI 314 stainless steel cylinder foams (Porvair[®], 60 ppi, diameter ~10 mm and height ~20 mm) were treated in a muffle at 900 °C for 2 h. The γ -Al₂O₃ support (Nyacol[®] AL20DW) was deposited by vacuum-assisted immersion. Further details were given elsewhere [24]. In order to investigate the influence of calcination temperature, the structured supports were calcined in static air at 550 °C or 700 °C for 2 h. Solutions (0.43 M) of the metallic oxide precursors (nickel and cerium nitrates) were used to incorporate the active metallic oxides to the alumina coating by cycles of immersion – blowing – drying (120 °C, 1 h) – calcination (550 °C, 4 h). This cycle was repeated until the final metal oxide loading of ~15 wt% was achieved. The structured catalysts were prepared under the form of Ni and Ni–Ce oxides. For the latter, the precursor solutions were prepared with Ce/Ni atomic ratios 0.11 and 0.25. The catalysts were named as indicated in Table 1.

2.3. Catalysts characterization

Crystalline phases of the different granulated catalysts were studied by X-ray diffraction (XRD). The analysis was performed with a Shimadzu XD-D1 diffractometer. Diffraction patterns were recorded using Cu K α radiation over a 2 θ –85° range at a scan rate of 1°/min, operating at 30 kV and 40 mA. The software package of the equipment was used for the phase identification. The estimated size of nickel oxide crystallite was calculated by the Scherrer equation. The plane used for the calculation of the crystallite size of nickel oxide was (200), corresponding to the main peak of NiO at 43.3° while for the calculation of cerium oxide crystallite the plane (111) corresponding to the main peak of CeO₂ at 28.6° was considered. The calculated values are an average of three FWHM measurements of the corresponding peaks in different XRD patterns.

The reducibility of nickel and cerium species for the granulated samples was analyzed by temperature-programmed reduction (TPR). The experiments were performed in an Ohkura TP-2002S instrument using a mixture of H₂/Ar (5%) as reducing gas. The heating rate was 10 °C/min from room temperature to 900 °C.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a multitechnique equipment (SPECS) with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV and Mg K α X-ray source power of 200 W. The pressure in the analyzing chamber was less than 5.9×10^{-7} Pa. The spectral regions corresponding to Ni 2p, Ce 3d and C 1s core levels were recorded for each sample. Peak fitting was performed with the CASAXPS software. The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mixture of Gaussian and Lorentzian functions.

The Raman spectra were recorded using a LabRam spectrometer (Horiba-Jobin-Yvon) coupled to an Olympus confocal microscope (a 100 \times objective lens was used for simultaneous illumination and collection), equipped with a CCD detector cooled to about –70 °C using the Peltier effect. The excitation wavelength was in all cases 532.13 nm (Spectra Physics diode pump solid state laser). The laser power was set at 30 mW.

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