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Additional Information

NiO diluted in high surface area TiO₂ as efficient catalysts for the oxidative dehydrogenation of ethane

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Abstract

Catalysts consisting of NiO diluted in high surface area TiO₂ can be as efficient in the oxidative dehydrogenation of ethane as the most selective NiO-promoted catalysts reported previously in the literature. By selecting the titania matrix and the NiO loading, yields to ethylene over 40% have been obtained. In the present article, three different titanium oxides (TiO₂) have been employed as supports or diluters of nickel oxide and have been tested in the oxidative dehydrogenation of ethane to ethylene. All TiO₂ used present anatase as the main crystalline phase and different surface areas of 11, 55 and 85 m² g⁻¹. It has been observed that by selecting an appropriate nickel loading and the titanium oxide extremely high selectivity towards ethylene can be obtained. Thus, nickel oxide supported on TiO₂ with high surface areas (i.e. 55 and 85 m² g⁻¹) have resulted to give the best catalytic performance although the optimal nickel loading is different for each case. The optimal catalyst has been obtained for NiO-loadings up to 5-10 theoretical monolayers regardless of the TiO₂ employed. Free TiO₂ is inactive whereas unsupported NiO is active and unselective (forming mainly carbon dioxide) and, therefore, unmodified NiO particles have to be avoided in order to obtain the optimal catalytic performance. The use of low surface area titania (11 m² g⁻¹) have led to the lowest selectivity to olefin due to the presence of an excess of free NiO particles.

Keywords: Ethylene; Oxidative dehydrogenation of ethane (ODH); Surface coverage; Titanium oxide; Nickel oxide.

1. INTRODUCTION

Ethylene, the main building block used in petrochemistry, has not been affected by the international crisis of the last decade. In fact, a continuous increase of the global capacity for ethylene production has been observed [1,2]. However, steam cracking, which is the current industrial process to produce ethylene, presents some drawbacks, such as low energetic efficiency [3,4] and low selectivity to the desired compounds. This has meant that many research groups have directed their efforts to find other alternatives. Among them we can highlight the oxidative dehydrogenation (ODH) of ethane, an exothermic reaction with just a few by-products easy to be separated [5,6,7,8].

At the moment the ODH of ethane has not been implemented in industry. However, there are promising results at lab- and pilot plant scale which suggest that this process can be developed in the mid-term. These results have been mainly obtained using either promoted nickel oxide [9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24] or Mo-V-O-based catalysts [25,26,27,28,29,30,31].

In the case of nickel oxide, the addition of promoters with certain characteristics is necessary to achieve high yields to ethylene [9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,32]. In this way, the presence of vacancies in NiO crystals have been proposed to be responsible for changes in the catalytic performance as it has been theoretically demonstrated by McFarland and Metiu [32].

Otherwise, in unpromoted NiO catalyst, the formation of CO₂ is remarkable and the selectivity to ethylene low [9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,32]. If basic dopants (elements with low valence, e.g. Na⁺, K⁺, Cs⁺) are incorporated as metal oxides, the valence state of the host element pushes towards its highest accessible valence. In contrast, acidic dopants (elements with high valence state, e.g., W⁶⁺, Nb⁵⁺, Sn⁴⁺) will push

the valence state of the host metal towards its lowest available valence. Thus, the addition of alkali elements increases the concentration of Ni^{3+} species while W^{6+} , Nb^{5+} or Sn^{4+} tends to maintain Ni^{2+} species [17]. By analyzing both the physico-chemical and the catalytic properties of NiO-based catalysts, it can be seen that non-stoichiometric nickel sites, Ni^{3+} , seems to be involved in non-selective reactions (CO_x formation), due to the stabilization of electrophilic oxygen species. Conversely, the elimination of these species means an enhancement in the ethylene formation [16,20,21,22].

Therefore, the nature of the promoter (with moderate acid characteristics and/or high oxidation state) has to be controlled in order to decrease the concentration of unselective non-stoichiometric Ni^{3+} species. In this way, Nb^{5+} and Sn^{4+} seem to be the most promising dopants.

Another possibility to improve the catalytic performance is by dispersing or diluting nickel oxide on a support. In this way a better dispersion of the active phase could be achieved when enhancing the number of available active sites. Among supports/diluters reported in the literature for NiO in ODH of ethane we can highlight MgO [12], zeolites [33,34] and Al_2O_3 [35,36,37,38,39,40].

The appropriate loading of diluted/supported NiO catalysts is different to that of promoted catalysts. In this regard NiO-loading must be remarkably lower in the case of diluted/supported catalysts, in order to achieve a Ni-diluter/promoter interaction similar to that obtained in NiO-promoted catalysts (usually prepared by co-precipitation) [40,41]. Unfortunately the catalytic performance of supported catalysts does not seem to be as good as that of promoted catalysts. Recently it has been reported that porous clays heterostructures can be efficient supports for NiO in the oxidative dehydrogenation of ethane, especially if these clays present columns made of titania [41]. Nanosized Ti–Ni–O catalysts prepared by a modified sol–gel method have also been investigated [42].

Different compositions were studied with the optimal composition showing yields to ethylene not higher than 12%. Recently, Zhu et al. [9] used a sol-gel method to synthesize NiO based catalysts promoted with W or Ti (with low amount of promoter, i.e. 5 wt% of metal promoter) observing high yields to ethylene, remarkably higher than those achieved over unpromoted NiO. Thus the incorporation of a second metal oxide to NiO drastically changes the structure and the catalytic properties.

In the present work several titanium oxides have been chosen as supports/diluters for nickel oxide. TiO₂ has been selected because it presents acidic characteristics and an oxidation state higher than +3 (i.e. Ti⁴⁺) which have been proposed to be beneficial for an optimal catalytic performance. The effect of the TiO₂ support, especially of the surface area, and the nickel oxide loading has been studied in detail.

2. EXPERIMENTAL

2.1. Preparation of catalysts

Three different titanium oxides have been used as diluters of nickel oxide: i) Pure anatase (Sigma-Aldrich), with low surface area (ca. 10 m² g⁻¹), and called as A; ii) TiO₂ (Degussa P25), mainly anatase (with low proportion of rutile), which presents medium surface area of ca. 55 m² g⁻¹, and called as B; and iii) Nanocrystalline anatase (Chempur APS 5 nm/ssa), with a surface area of 150 m² g⁻¹, was calcined in air at 500°C, then decreasing its surface area to 85 m² g⁻¹. This titania has been called C. Different amounts of nickel oxide have been deposited on each titanium oxide (Table 1).

Diluted NiO/TiO₂ catalysts were prepared through the evaporation at 60 °C of a stirred ethanolic solution of nickel nitrate, Ni(NO₃)₂•6H₂O (Sigma-Aldrich) and oxalic acid (oxalic acid/Ni molar ratio of 3) to which the corresponding titanium oxide was added. The solids obtained were dried overnight at 120 °C and finally calcined for 2 h at 500 °C.

The catalysts have been named as xNi-Y, x being the theoretical NiO wt% loading and Y the diluter employed (i.e. A, B or C).

2.2. Characterization of the catalysts

Surface areas were determined by multi-point N₂ adsorption at -196 °C. The data were treated in accordance with the BET method.

Powder X-ray diffraction (XRD) was used to identify the crystalline phases present in the catalysts. An Enraf Nonius FR590 sealed tube diffractometer, with a monochromatic CuK α 1 source operating at 40 kV and 30 mA was used.

Morphological, compositional and structural analysis the samples were performed by high resolution transmission electron microscopy (HRTEM) with a field emission gun TECNAI G2 F20 microscope operating at 200 kV, having the capabilities of selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX). The elemental composition and distribution of nickel have been determined using EDX-mapping. In order to prepare the TEM specimens, powdered samples were sonicated in absolute ethanol for several minutes. A drop of the resulting suspension was deposited onto a holey carbon film supported on a copper grid, which was subsequently dried.

Temperature-programmed reduction (H₂-TPR) was carried out in a Micromeritics Autochem 2910 equipped with a TCD detector, in which the reducing gas was 10% H₂ in Ar (total flow rate of 50 ml min⁻¹). The temperature range explored was from room temperature to 800 °C. The heating rate was maintained at 10 °C min⁻¹.

The chemical characterisation of the surface of the samples was performed by XPS analysis. A Physical Electronics spectrometer (PHI 5700) with X-ray Mg K α radiation (300W, 15 kV, 1253.6 eV) as the excitation source was used for high-resolution record. Measurements were performed by a concentric hemispherical analyser operating in the

constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Under these conditions, the Au $4f_{7/2}$ line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. Charge referencing was done against adventitious carbon at 284.8 eV. Each spectral region was scanned performing several sweeps, until a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 5×10^{-6} Pa. PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves and following the methodology described in detail elsewhere [23,43]. Atomic concentration percentages of the characteristic elements of the surfaces were determined taking into account the corresponding area sensitivity factor [43] for the different measured spectral regions.

Diffuse reflectance UV–Vis spectra were collected on a UV-2600 Shimadzu equipped with a “Praying Mantis” attachment from Harrick. The sample cell was equipped with a heater unit, a thermocouple, and a gas flow system for in situ measurements. The samples were dehydrated in situ in dry air at 150°C for 30 min.

2.3. Catalytic test for ethane oxydehydrogenation

The catalytic tests in ethane oxidation were carried out in a tubular isothermal flow reactor in the 300–500 °C temperature range. The feed mainly corresponds to a mixture consisting of $\text{C}_2/\text{O}_2/\text{He}$ with a molar ratio of 3/1/26, although $\text{C}_2/\text{O}_2/\text{He}$ molar ratio of 3/3/24 was also used in a few cases. Both the catalyst amounts loaded and the total flows used were largely varied in order to get different contact times and finally to achieve different ethane conversions at a given reaction temperature. Samples were introduced in the reactor

diluted with silicon carbide in order to keep a constant volume in the catalytic bed. Reactant and products were analyzed by gas chromatography using two packed columns: (i) molecular sieve 5 Å (2.5 m); and (ii) Porapak Q (3 m). Blank runs showed no conversion in the range of reaction temperatures employed.

3. RESULTS AND DISCUSSION

3.1. Catalytic results in the oxidative dehydrogenation of ethane

NiO supported or diluted in TiO₂ has been tested in the oxidation of ethane and the catalytic results obtained indicate that these catalysts are very efficient for the production of ethylene although the catalytic results depend on both the nature of the titania used and the loading of nickel oxide (Table 1). In all cases, ethylene has been the main reaction product and CO₂ was also detected as minority. However, neither CO nor other partially oxygenated compounds were identified.

In this article we want to study not only the influence of the diluter but also the influence of the nickel loading on the catalytic performance. Thus, Figure 1a shows the selectivity to ethylene obtained at 450 °C for an ethane conversion of 10% (using different contact times but keeping the C₂/O₂/He ratio constant) for the different catalysts studied. In all cases, the selectivity to ethylene over NiO-TiO₂ catalysts is remarkably higher than that achieved over pure NiO (ca. 45%). However, selectivity to ethylene values highly vary depending on the characteristics of catalysts (i.e. Ni-loading and/or support). As it can be seen the optimal selectivity is obtained at low and especially at intermediate NiO contents although it is observed that the preferred amount of NiO depends also on the diluter, in a way that the higher the surface area of the diluter the higher the optimal Ni-loading is.

The overall highest selectivity to ethylene has been obtained using titanium oxide of both intermediate (Ni-**B** series) and high (Ni-**C** series) surface area, reaching in the best cases

90% selectivity to ethylene at 10% ethane conversion. This value has been obtained by catalysts with NiO contents of ca. 20-50 wt% for Ni-B series and ca. 50 wt% for Ni-C series. On the other hand, the most selective catalyst using the low surface area support (Ni-A series) presents a NiO-loading from 4 to 20 wt% NiO, although the selectivity to ethylene is only 65-70%.

Figure 1b shows the evolution of the selectivity to ethylene with the ethane conversion at 450°C for some representative catalysts focusing on those with 20 wt% NiO. As can be seen the decomposition of ethylene is moderate for all NiO/TiO₂ catalysts tested.

The catalytic activity was also very different for the catalysts tested. Table 1 shows the ethane conversion obtained with these catalysts. It can be seen that the catalytic activity for a fixed nickel loading varies for the different titania supports. In spite of the fact that the amount of the supposedly active sites (NiO species) was the same in all cases the conversions achieved are different. Thus, the most active catalyst was the one based on the low surface area (A support) and the catalytic activity decreases with increasing the surface area of the support.

Data shown until now in the present work have been obtained in an O-poor atmosphere (C₂/O₂/He = 3/1/26; O₂/C₂=1/3 molar ratio). Therefore the ethane conversion is highly limited as we would run out of oxygen and this would modify the nature and oxidation state of nickel. Due to this we also used O-richer feed (C₂/O₂/He = 3/3/24; O₂/C₂=1/1 molar ratio) to be able to reach higher conversions [44]. This way, we have achieved an ethylene yield of ca. 41% (ethane conversion = 55.2%, selectivity to ethylene = 73.9%) at 450 °C on 50Ni-B catalyst, at 450°C and using a contact time, W/F, of 16 g_{cat} h⁻¹ (molC₂H₆)⁻¹. By optimizing the catalytic conditions this value could be improved.

3.2. Characterization results of NiO/TiO₂ catalysts

Since these catalytic results could be related to the higher/lower concentration of NiO crystallites which are not interacting with titania supports, the catalysts have been characterized by several physicochemical techniques in order to explain the catalytic results. Table 2 shows some characteristics of these catalysts.

Figure 2 presents the XRD powder patterns of the most representative NiO/TiO₂ catalysts (the remaining XRD results are shown, as supplementary information, in Figs. S1 to S3, for A-, B- and C-series of catalysts, respectively). TiO₂ anatase was only observed in the Ni-A- and Ni-C-series supported catalysts whereas TiO₂ anatase, with low amount of TiO₂ rutile, was observed in catalysts of Ni-B-series. As expected, the relative intensity of the crystalline titanium oxides phases compared to NiO decreased when increasing the Ni-content of the catalysts. Regarding to the Ni-species detected, NiO crystallites were the only one observed. No mixed Ni-Ti-O phases are apparent.

For a more comprehensive knowledge about the influence of the morphology and crystallite size on the catalytic performance, a detailed microscopy study has been conducted. Figure 3 presents transmission electron micrographs of some representative supported NiO samples on different TiO₂ materials. In general, as we can observe in Figure 3, all samples consist of nearly spherical nanoparticles although with variable crystal sizes, mainly ranging from 4 to 50 nm. The changes in crystal grain sizes and morphology of samples were related to both the Ni-content and the nature of the TiO₂ matrix.

As shown in TEM image (Fig. 3a), **4Ni-A** sample is composed of small NiO nanoparticles (NPs) with size ranging from 4 to 12 nm which are spread over the surface of large titania particles of 40 to 250 nm. However, an increase in the density of the NiO nanoparticles as well as a small increase in grain size can be observed when the Ni-loading increases (**20Ni-A** sample, Fig. 3b); the measured diameter of NiO NPs was found to be in the 5-

15 nm range. In **20Ni-A** the area of the TiO₂ matrix covered by NiO NPs is higher than that of **4Ni-A**. Moreover, in **20Ni-A** sample, it is also seen that there are a few aggregations of NiO nanoparticles which are not in contact with TiO₂.

If the surface area of the TiO₂ matrix increases a different trend is observed. Thus, for **20Ni-B** (Fig. 3c) an increase in size and density of NiO nanoparticles is observed (which is also accompanied with a decrease in the area of free titania matrix). It seems that the size of TiO₂ crystals in the case of support A was about 40-250 nm while in the case of support **B** the size of TiO₂ crystals was reduced (ranging from 20 and 100 nm).

In the case of the sample **20Ni-C** (with the matrix presenting the highest surface area), it is observed that the size of NPs increases (ranging from 10 to 33 nm). These domains mainly present a core-shell structure in which the TiO₂ matrix is covered by NiO. Moreover, some uncovered or only partly covered TiO₂ particles were also observed. The EDX analysis shows an irregular composition and, depending on the analyzed area, a richer or poorer Ni concentration is observed, which is in agreement with the corresponding TEM images. In the case of the catalyst with higher Ni-loading, i.e. sample **50Ni-C**, a clear increase in NPs size which are in the 20-35 nm range is observed (Fig. 3d). Moreover, the NPs density drastically increases, resulting in a total coverage of TiO₂ matrix by NiO particles presenting a higher thickness than that observed in **20Ni-C**. The NiO NPs distribution was not homogenous and the Ni content measured by EDX, depending of the analyzed area varied between 30 and 100 at %. This is in accordance with the images obtained in which a few agglomerations of NiO particles which are not in contact with the TiO₂ matrix are also observed. At higher Ni-loading, **80Ni-C**, a similar scenario was observed but with a higher concentration of agglomerations of TiO₂-free NiO particles. Fig. 3f shows a representative EDX spectrum of a single NiO nanoparticle on titania matrix, in which Ti, Ni and O atoms are the only elements detected (apart from

copper and carbon from copper grid employed). In order to determine the Ni-O crystalline phases of the sample; SAED patterns were recorded and indexed from prepared samples. SAED patterns (Fig. 3e) show several concentric rings formed by clear small spots; which indicates that these samples consist of small NiO crystalline nanoparticles. The measured interplanar distance from diffraction rings were about 0.243, 0.209, 0.149, 0.127 and 0.122 nm and could, respectively, be attributed to (111), (200), (220), (311) and (222) planes of NiO. SAED patterns of NiO were indexed to Face-centered cubic phase structure space group Fm3m of NiO (JCPDS: 01-78-0643).

On the other hand, and in order to confirm the size and distribution of NiO nanoparticles, additional measurements in Dark field (DF-TEM) mode were made (Figs. S4, Supporting Information). Conventional DF-TEM imaging was achieved by selecting and inserting a small objective aperture around (111) and (002) diffraction spots from SAED pattern. It can be seen that, in the case of 4Ni-A sample, NiO nanoparticles are well dispersed with sizes ranging from 4 to 12 nm, as mentioned above (Figs. S4, Supporting Information).

Figure 4 shows a high resolution TEM image of NiO nanoparticles with size 4-10 nm in 4NiA sample. The measured interplanar distance HRTEM micrograph were about 0.241 nm and 0.208 nm corresponding to the (111) and (200) planes respectively. The FFT pattern (not shown) was indexed to face centered cubic phase structure of NiO, which is in good agreement with the results obtained by SAED and confirms the nature of nickel oxide nanoparticles. Modifications in crystal lattice parameter could give some indications about crystal size and structure disruptions. In order to check this, the mean value of the *a*-lattice parameter of NiO was determined for some representative catalysts from (111), (200) and (220) orientations (Table 2). As we can observe some variations in the lattice parameter are observed which could be related to the crystallite size of NiO NPs, as well as to the distribution over the TiO₂ matrix.

Catalysts in C-series as well as samples with NiO content of ca. 20 wt% (i.e. **20Ni-A**, **20Ni-B**, **20Ni-C**) were analyzed by XPS (Figure 5) and their main surface features are summarized in Table 3. As it can be noted, the resulting surface composition is higher than that given by the bulk chemical composition of the catalysts, which would result in a Ni/(Ni+Ti) ratio of 0.20 (Table 3). In this regard, **20Ni-A** catalyst leads to a surface Ni/(Ni+Ti) ratio of 0.28, while samples **20Ni-B** and **20Ni-C** present 0.46 and 0.54 ratios respectively. These results are in agreement with TEM studies performed on the samples, in which NiO species are worse dispersed over the low surface area support A, which also presents not covered TiO₂ particles, facts that would lead to a lower Ni concentration at the surface. This effect is even higher for catalysts in C-series, which present the highest surface area support. Accordingly **10Ni-C** sample shows the triple Ni concentration at the surface than that expected from its chemical composition.

Ni 2p core level spectra show a main line together with a satellite structure (SII) ca. 7 eV higher BE, which has been associated to a ligand-metal charge transfer (the shake-up satellite) [45,46,47]. Also a peak broadening over the main line can be observed, fact that suggests the presence of another satellite peak (SI) at ca. 1.5 eV higher BE, which has been ascribed to the presence of several defects and Ni species such as, Ni²⁺ vacancies [46], Ni²⁺-OH [47], Ni³⁺ ions [48] or Ni²⁺ surface interactions [49]. Another weak intensity line at lower BE attributed to differential charging of the samples is present in the examined materials (asterisk in Figure 6). Ni 2p_{3/2} main peak is in the range 853.6-854.3 eV which corresponds to a Ni²⁺ oxidation state in an environment ranging from pure NiO to Ni(OH)₂ [50]. On the other hand, some differences on the satellite/main line intensity ratios can be noted (Table 3). Not significant changes have been observed in the SI/main peak ratio, however SII/main peak ratio increases on samples **20Ni-B** and **20Ni-C** (Table 3). These differences can be related to an enhancement in the non-local

screening process, associated to the concentration and the number of surface cation vacancies, to particle size and structural transitions [45].

Figure 6 shows H₂-TPR profiles of the NiO-TiO₂ catalysts, whereas Table 2 summarizes both the H₂-uptake and temperature of the maximum H₂ consumption (TMC) in the H₂-TPR experiments. For a suitable assignment of the reduction bands, TPR experiments were also conducted on the pure titania supports. No reduction band was observed and the consumption of hydrogen detected was negligible. Accordingly, the reductions observed in NiO-TiO₂ catalysts are assigned to nickel species. It can be seen that as nickel content increases in each series the temperature of the maximum H₂ consumption (TMC) slightly shifts to higher temperature values, regardless of the nature of the titania support used. Generally NiO TPR-profiles consist of two reduction bands, corresponding to two types of NiO-species that reduce to metallic nickel; either particles which present different oxide-support interaction, or Ni species with different oxidation state [51,52,53]. Taking into account that no clear evidences of the presence of Ni³⁺ were obtained by XPS, the signal appearing at lower temperatures (250-300 °C) can be attributed to NiO particles which present low dispersion over the support, while the signal appearing at higher temperatures (300-500 °C) can be assigned to better dispersed NiO species [53]. Therefore, for a fixed NiO content (20% wt) the TMC shifts from 328 to 291 °C, as the surface area of the support increases (Fig.6.b, d, g). The same trend is observed at lower NiO contents, in which reduction temperature shifts from 308 to 266 °C (Fig.6, patterns a, c and f).

DR-UV-Vis. spectra were conducted on representative catalysts in order to observe the degree of dispersion of Ni²⁺ species on titania (Fig. S5, supplementary information). The first observation of the spectra lead us to the conclusion that a high intensity band between 220 and 400 nm is detected for all catalysts, and the size of this band decreases when the

nickel-loading increases. Thus, it indicates that this band is mainly linked to the presence of TiO₂ anatase, specifically due to the charge transfer from O 2*p* valence band to Ti 3*d* conduction band, as reported elsewhere [54]. Bands at 450 and 515 nm have been related to the presence of Ni-Ti-O species (charge transfer from Ni²⁺ to Ti⁴⁺ [55]) but in none of the catalysts tested here have been clearly appreciated. However, a band at ca. 560 nm and a shoulder at ca. 640 nm which can be related to less dispersed NiO on the titania are observed in some of the catalysts, but not in the pure supports. Finally a band at ca. 720 nm which is due to the presence of bulk NiO particles [56] is present in all the Ni-containing samples and increases with the nickel loading. Unfortunately, not an accurate information can be drawn from the DR-UV-Vis. study since in the 220-450 nm range the absorption of Ni species are overlapped by more intense bands related to the TiO₂ support.

3.3. General remarks

In this work it has been observed that the nature of the titania employed as a support of nickel oxide defines the catalytic performance. Thus, it seems that medium and high surface area titania are the appropriate supports whereas low surface area titania leads to considerably less selective catalysts. On the other hand, if high NiO loading is present in the catalysts a decrease in the olefin formation is also observed compared to the optimal catalysts. Therefore, two factors must be controlled, i.e. the nature of titania and the nickel loading.

The low selectivity obtained by the catalysts supported on the low surface area titania (support A) must be due to the low amount of domains in which titania and NiO are in contact. According to the TEM results these catalysts are formed to a high extent by free TiO₂ particles and free NiO crystallites. Thus the amount of unselective NiO crystallites

which are not modified by titania is high, and consequently the selectivity to ethylene low. The microscopy results can be confirmed by XPS. Thus, for the catalyst with 20 wt.% NiO on the low surface area titania (**20Ni-A**) the surface Ni/(Ni+Ti) atomic ratio is 0.28 which is only slightly higher than that of the bulk composition (0.21). However, in the catalysts with the same NiO loading but with the supports with higher surface area (i.e. **20Ni-B** and **20Ni-C** catalysts) the Ni/(Ni+Ti) atomic ratio increases up to 0.46-0.50, respectively, demonstrating higher interaction/dispersion of nickel oxide with the titania. The same reasoning can be applied to the catalysts with high Ni-loadings. Thus, if the NiO loading is too high the olefin formation decreases and this must be due, as detected by TEM analyses, to the presence of unmodified NiO which alone presents a low selectivity to the olefin.

Figure 7 shows the variation of the selectivity to ethylene (at fixed conversions and reaction temperature) with the theoretical coverage of the titania. The theoretical coverage of NiO (Table 2) has been calculated from reference [57], in which the monolayer of NiO has been estimated to be 0.12 g / 100 m² of support. In all cases a similar trend is observed, with the optimal performance obtained at until 5-10 monolayers. Thus NiO catalysts diluted in TiO₂, presenting NiO crystallite with some interaction with TiO₂ particles, are highly efficient, whenever an excess of unmodified NiO is not achieved.

Anyhow, according to TEM results (and depending on both nickel oxide loading-and the TiO₂ support), the distribution of nickel oxide and titanium oxide is not that of a typical TiO₂-supported NiO catalyst (i.e. TiO₂ support and, over it, a variable number of nickel oxide layers). In fact we can see a heterogeneous mixture of: i) core/shell agglomerations with TiO₂ particles inside and NiO particles outside; ii) free NiO particles; iii) free TiO₂ particles; and iv) some agglomerations of particles with Ni species spread over the titania.

The optimal supported NiO/TiO₂ catalysts studied in the present article have a catalytic performance at the same level that the most efficient promoted NiO catalysts reported in the literature for the oxidative dehydrogenation of ethane [16, 20]. It has been demonstrated that using a diluter as high surface area TiO₂ it is possible to achieve similar performance than promoted NiO catalysts. However, the amount of promoter (i.e. Nb₂O₅, SnO₂) or diluter (TiO₂) which leads to the optimal performance is very different. Thus for promoted NiO-catalysts prepared by co-precipitation just a low amount of promoter is required whereas a higher amount of diluter/support is required in the diluted/supported catalysts prepared by wet impregnation.

Moreover, we have observed that these catalysts present a good stability. A representative catalyst, **20Ni-B**, was studied for 26 h using invariable reaction conditions. Thus, after a slight decrease in the ethane conversion for the first 2-3 h the activity remained stable for the following 20 h. Regarding to the selectivity to ethylene, just a subtle increase was observed for the first hours of experiment and then no significant changes were appreciated (Fig. S6, supplementary information). The surface area of the catalyst used in the stability test was measured, slightly decreasing from 50.4 m² g⁻¹ in the fresh sample to 46.2 m² g⁻¹ (see Table S2). This drop can be related to the decrease of the catalytic activity observed. An analysis of the carbon present in the catalyst shows that the amount of C on the surface is very low for both fresh and used catalysts. Thus, the deposition of carbon on the surface does not seem to be related to this deactivation.

As mentioned above the catalytic performance in terms of conversion/selectivity to ethylene of these NiO/TiO₂ catalysts is in the range of the best materials reported. Additionally, the productivity to ethylene per gram of catalyst achieved is high but the productivity per gram of nickel is more notorious, as in this case our catalysts present a high proportion of support/diluter, in contrast with more recently promoted NiO catalysts,

which are predominantly nickel oxide with low amounts of the promoter oxide [10-24]. Thus, in Table 4 catalytic data in the ODH of ethane of some representative catalysts reported in the literature based on NiO are shown. As it can be seen **20Ni-B** (with only 20 wt% NiO) achieves productivity towards ethylene of ca. $2500 \text{ g}_{\text{C}_2\text{H}_4} \text{ kg}_{\text{Ni}}^{-1} \text{ h}^{-1}$, remarkably higher than those of the other catalysts shown. It must be noted that our data has been drawn at 450°C which is a higher temperature than in most of the other data presented in Table 4.

Conclusions

NiO diluted in TiO_2 can be as efficient in the oxidative dehydrogenation of ethane as the most selective NiO-promoted catalysts reported previously in the literature, with the advantage of requiring lower amount of nickel in the catalyst composition, which could mean lower sintering and better physical properties. In this work, yields to ethylene over 40% have been achieved, which could be improved by selecting suitable reaction conditions. Over NiO diluted in TiO_2 catalysts selectivity to ethylene over 90% can be achieved at 10% conversion and that selectivity decreases only slightly by increasing the ethane conversion. A selection of both the nickel loading and the titanium oxide support is required to obtain the optimal catalytic results. Thus, TiO_2 with high surface areas (55 and $85 \text{ m}^2/\text{g}$) have resulted to give the best catalytic performance although the optimal nickel loading is different for each case. The design of the catalysts must be done in a way that the presence of unmodified NiO sites is minimal in order to achieve the best catalytic results.

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Caption to figures

Fig. 1. Catalytic performance of NiO/TiO₂ catalysts: a) Variation of selectivity to ethylene (at ethane isoconversion of 10%) with the NiO-loading for catalysts of Ni-A-, Ni-B- and Ni-C-series; b) Variation of selectivity to ethylene with ethane conversion at different contact times, W/F, in the range of 1-12 g_{cat} h⁻¹ mol_{C₂}⁻¹.

Fig. 2. XRD patterns of representative NiO/TiO₂ catalysts.

Fig 3: Representative TEM images of (a) 4Ni-A; (b): 20Ni-A; (c) 20Ni-B; and (d) 50Ni-C. Photographies (e) and (f) correspond to SAED pattern and EDX spectrum, respectively, recorded from 20Ni-C sample. Scale bar is 100 nm.

Fig. 4. High resolution TEM image of NiO nanoparticles in (a) 4Ni-A and (b) 20Ni-B samples.

Fig. 5. Ni 2*p* core level spectra of the 20% wt. NiO-TiO₂ catalysts: a) 20Ni-A, b) 20Ni-B and c) 20Ni-C.

Fig. 6. H₂-TPR profiles of catalysts for Ni-A- (patterns a and b), Ni-B- (patterns c to e) and Ni-C-series (patterns f to h) series: a) 4Ni-A; b) 20Ni-A; c) 2Ni-B; d) 20Ni-B; e) 50Ni-B; f) 10Ni-C; g) 20Ni-C; h) 50Ni-C.

Fig. 7. Variation of the selectivity to ethylene with the theoretical NiO coverage (fixed conversion $\approx 10\%$). Note: Reaction temperature = 450°C , $\text{C}_2\text{H}_6/\text{O}_2/\text{He}$ with a molar ratio of 3/1/26.

Table 1. Catalytic properties of NiO/TiO₂ catalysts for the oxidative dehydrogenation of ethane at 450°C.^a

Catalyst	NiO loading wt. %	Ethane Conversion (%) ^b	Selectivity, %		Activation Energy, KJ mol ⁻¹
			Ethylene	CO ₂	
1Ni-A	1	0.7	61.8	38.2	88.8
4Ni-A	4	4.1	63.0	37.0	85.5
10Ni-A	10	12.5	66.1	34.0	87.0
20Ni-A	20	18.7	64.1	35.9	76.4
50Ni-A	50	19.1 ^c	61.8	38.2	81.9
2Ni-B	2	3.2	86.2	13.8	76.4
5Ni-B	5	6.4	84.7	15.3	81.2
10Ni-B	10	8.9	86.4	13.6	82.8
20Ni-B	20	11.9	89.3	10.7	92.0
50Ni-B	50	15.9	87.0	13.0	95.5
80Ni-B	80	16.3 ^c	75.5	24.5	82.4
10Ni-C	10	2.9	84.2	15.6	84.5
20Ni-C	20	4.8	86.5	13.5	82.3
35Ni-C	35	13.6	84.8	15.2	87.7
50Ni-C	50	14.0	89.8	10.2	74.5
80Ni-C	80	17.2 ^c	85.4	14.6	86.4
NiO	100	7.5 ^c	42.0	58.0	n.d

^a Reaction conditions detailed in the experimental part of the text.

^b Contact time, W/F, of 4.0 in g_{cat} h (mol_{C₂H₆})⁻¹.

^c Contact time, W/F, of 2.0 in g_{cat} h mol_{C₂H₆})⁻¹.

Table 2. Physicochemical characteristics of NiO/TiO₂ catalysts.

Catalyst	Surface area m ² g ⁻¹	Coverage ^a		a-lattice parameter NiO crystallites ^b	TPR- results	
		10 ⁻³ gNiO/m ²	Layers		H ₂ -uptake(mmol/g)	TMC ^c
4Ni-A	n.d.	3.8	3.2	4.167	0.80	308
20Ni-A	25.6	22.9	19	4.209	3.84	321
2Ni-B	53.9	0.41	0.34	n.d.	0.89	297
20Ni-B	50.4	5.0	4.2	4.220	3.65	298
50Ni-B	46.6	20.0	17	n.d.	12.27	337
80Ni-B	51.4	80.0	67	n.d.	14.04	296
10Ni-C	80.1	1.3	1.1	n.d.	2.46	266
20Ni-C	65.4	2.9	2.5	4.195	3.74	291
50Ni-C	73.8	11.8	9.8	4.216	8.65	337

^a g NiO per m² of the original support, Layers indicate the number of theoretical layers of NiO on titania by supposing the monolayer to be 0.0012 gNiO m⁻²;

^b mean a-lattice parameter, in Å, observed for the NiO crystallites determined by TEM;

^c temperature, in °C, of the maximum hydrogen consumption.

Table 3. XPS results for selected NiO/TiO₂ catalysts.

Sample	Ni/(Ni+Ti)		Ni 2p _{3/2} (eV)			O 1s (eV)	
	Bulk (EDX)	Surface (XPS)	Main peak	Sat I/Main peak	Sat II/ Main peak	O _α	O _β
20Ni-A	0.21	0.28	853.6	1.33	0.84	529.9 (94%)	531.7 (6%)
20Ni-B	0.21	0.46	853.9	1.58	1.99	529.9 (94%)	532.4 (6%)
50Ni-B	0.50	0.54	854.3	1,04	0.75	530.0 (86%)	531.8 (14%)
10Ni-C	0.11	0.32	854.0	1.55	1.64	530.1 (87%)	532.6 (13%)
20Ni-C	0.21	0.54	854.3	1.51	1.74	529.9 (91%)	532.5 (10%)
50Ni-C	0.51	0.71	854.2	1.38	1.38	529.7 (82 %)	532.5 (18%)

Table 4. Representative results reported in the literature for the oxidative dehydrogenation of ethane on Ni-based catalysts.

Catalyst	C ₂ /O ₂ /inert molar ratio	T /°C	W/F ^a /g s cm ⁻³	C ₂ conv. ^b /%	Y _{C₂} ^c /%	Productivity ^d		Ref.
						per kg of catalyst	per kg of Ni	
NiNbO	9.1/9.1/81.8	400	0.54	66	46	319	375	20
NiNbTaTiO	80/5/15	275		15	13			58
NiTaNbO	50/10/40	300	3.1	16	13	85	100	59
NiWO	10/10/80	400	0.6	52	31	210	221	9
NiTiO	10/10/80	400	0.6	50	33	222	234	9
NiCeO	10/3.3/86.7	275	1.15	8	5	18	24	15
NiNbO/Al ₂ O ₃	9.1/9.1/81.8	400	0.6	27	19	131	438	39
NiO/Al ₂ O ₃	10/10/80	450	1.06	59	39	149	648	36
50Ni-B	10/10/80	450	0.23	55	41	728	1456	This work
20Ni-B	10/10/80	450	0.23	41	30	518	2589	This work

^a pseudo-contact times (W/F) equivalent to the weight of catalyst (g) divided by the feed gas flow rate at operating conditions (cm³ s⁻¹);

^b conversion of ethane;

^c per pass yield of ethylene;

^d productivity to ethylene in g_{C₂H₄}/(kg_{cat}.h) or g_{C₂H₄}/(kg_{Ni}.h).

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