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Additional Information

Distortion of the NiO crystal lattice in porous clay heterostructures enhances the selectivity in the oxidative dehydrogenation of ethane

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Abstract

Porous Clay Heterostructures (PCH) have shown to be highly efficient supports for nickel oxide in the oxidative dehydrogenation of ethane. Thus NiO supported on silica with PCH structure shows productivity towards ethylene three times higher than if NiO is supported on a conventional silica. This enhanced productivity is due to an increase in the catalytic activity and especially to a drastic increase in the selectivity to ethylene. Additionally, PCH silica modified with columns of TiO₂ have also been synthesized and used as supports for NiO. An enhanced activity and selectivity to ethylene was found compared to the TiO₂-free PCH. The enhanced catalytic performance has been related to the high dispersion of nickel oxide particles on the support, which leads to a lower reducibility of the nickel oxide, hindering the oxidation of ethane into carbon oxides. More interestingly, the particle morphology plays an important role on the catalyst selectivity since **a higher distortion of the NiO crystal lattice parameter has meant an enhanced selectivity to ethylene.**

Keywords: NiO crystal lattice; Porous Clay Heterostructures; nickel; Oxidative Dehydrogenation of ethane (ODH); ethylene.

1. INTRODUCTION

Ethylene is the most important raw material in petrochemistry. Indeed, final products such as polyethylene, vinyl chloride and polystyrene have their origin in ethylene. Demand of ethylene has been growing for the past years in spite of the global crisis that affected most of the developed countries. In fact, at the beginning of 2014 the global capacity for ethylene production was 146 millions tpy, which is 1.8% higher than in 2013 and 3.5% higher than in 2012.¹ This growth has been mainly localized in the Asian and the Middle Eastern companies.² Nowadays most of the ethylene is produced via steam cracking, an inefficient process from an energetic viewpoint.³ Therefore the search for alternatives to produce ethylene in a more energetically favorable way is highly interesting. Thus, oxidative dehydrogenation (ODH) of ethane is considered as a viable and interesting alternative for the industrial manufacture of ethylene.⁴⁻⁷

Currently, two catalytic systems are the most promising in the ODH of ethane, those based on Mo-V-Me-O oxides⁸⁻¹⁴ and those based in nickel oxide.¹⁵⁻³¹ In the present work we will focus on catalysts based in nickel oxide. It is known that NiO alone can easily activate ethane with high activity. Unfortunately ethane is mainly transformed into carbon dioxide with low olefin formation.^{15,19} However, if NiO is modified by either using appropriate metal oxides as supports or, especially, using suitable promoters added in the preparation procedure the production of ethylene can be largely enhanced.¹⁵⁻³¹

The use of catalytic supports is usually highly beneficial because it favors the dispersion of the active phase, enhancing the number of available active centers, and also, in most cases, modifies the nature of the active sites. NiO based catalysts have been tested in ODH reaction using several supports such as MgO,¹⁷ CeO₂,²⁰ zeolite^{24,25} and mainly Al₂O₃;²⁶⁻²⁸ better catalytic performance in terms of activity and especially selectivity to

olefin have been reported in supported NiO catalysts than in bulk NiO. In this way, it has been recently suggested that small NiO crystallites tend to produce more ethylene than large NiO crystallites, which is favored by using metal oxides support with acid characteristics.²²

Clay minerals are versatile materials with a wide range of applications and low cost, among them, these materials have been used as catalysts and catalytic supports. The applications of the clay minerals can be influenced by the physicochemical properties of them. The clay minerals can improve their textural properties mainly through two methods. Pillared Interlayer Clays (PILCs) are synthesized by the insertion of pillaring agents, mainly inorganic complexes, which expand the interlayer spacing leading to a porous framework with high micro- and mesoporosity. However, the relative low thermal stability limits its application. Porous Clay **Heterostructures** (PCHs) are other structures synthesized using another method to incorporate pillars between two adjacent layers which are based on the ionic exchange of the cations of the clay by a bulky cation to increase the interlayer spacing and subsequent formation of the pillars by the addition of silicon source. This procedure leads to porous materials with high surface area.

It has been described in the literature that the incorporation of a low proportion of heteroatoms as aluminium,³² zirconium³³ or titanium³⁴ can improve the acid properties of the PCHs and the thermal stability giving rise to materials with potential interest for catalytic applications.

In the present article, the use of a silica with a Porous Clay Heterostructure as support of nickel oxide will be studied for the ODH of ethane, and its performance will be compared with that obtained by conventional silica as support. PCH structures present a high surface area that can be useful for a better dispersion of nickel oxide on its surface.

Other formulations of the PCH structure can be synthesized by changing the silica columns by the incorporation of other heteroatoms; however this preparation is not always successful because the incorporation of a high content of heteroatoms can lead to the delamination of the montmorillonite or the collapse of the porous structure. Thus, PCH-silica with the incorporation of titania as the constituent of the columns has been reported to be feasible³⁴ and also presents an acidic character which could be favorable for nickel oxide based catalysts to be applied in the oxidative dehydrogenation of ethane.²²

2. EXPERIMENTAL

2.1. Preparation of supports and catalysts

The raw mineral used in this work was a bentonite from “Sierra de Níjar” (Spain) that was supplied by Minas de Gador S.A. The bentonite shows a high proportion of montmorillonite as reported in previous studies.³⁵

Prior to the synthesis to the PCH, the montmorillonite phase was collected by sedimentation and treated with a solution of NaCl for 1 day to obtain the homoionic montmorillonite (Na-mont).

5 g of Na-mont were treated with a saturated solution of 27 g of hexadecyl trimethyl ammonium bromide (HDTMBr) (Sigma-Aldrich) in 200 ml of *n*-propanol (VWR), leading to an ionic exchange between Na⁺ and HDTM⁺ and expanding the interlayer spacing. After 3 days, the solution was filtered until neutral pH to remove the excess of the HDTM⁺. After that, the solid was recovered and redispersed in 500 ml of H₂O for 1 day and then a solution of 1-hexadecylamine (1.8 g) in *n*-propanol (50 ml) was added to the first solution and stirred for 1 day. Si-pillars and Si/Ti-pillars (with a molar ratio of Si/Ti=5) were dispersed in a solution of *n*-propanol with a ratio Si/*n*-propanol or

(Si+Ti)/*n*-propanol equal to 1 and added to the first solution, maintaining the stirring for 3 days. The source of silicon and titanium were tetraethyl orthosilicate (Aldrich) and tetrapropyl orthotitanate (VWR), respectively. Finally, the gel was filtered and washed with water and ethanol and dried at 60 °C in air for 12 h. Finally the surfactant was removed by the calcination at 550 °C with a rate of 1 °C min⁻¹ during 6 h. Thus, samples with Si-pillars or Si/Ti-pillars will be named as PCH or PCH-Ti, respectively.

Supported NiO 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 to which the corresponding support (conventional silica, PCH or PCH-Ti) 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 xNiSi when the support employed was conventional silica ($S_{\text{BET}} = 181 \text{ m}^2 \text{ g}^{-1}$), xNiPCH when the support was pillared with silica ($S_{\text{BET}} = 644 \text{ m}^2 \text{ g}^{-1}$) and xNiPCH-Ti when the support was pillared with silica-titania ($S_{\text{BET}} = 562 \text{ m}^2 \text{ g}^{-1}$); **x stands for the theoretical NiO wt.% loading.**

2.2. Characterization of the catalysts

Morphological, compositional and structural analysis of mixed oxides samples were performed by high resolution transmission electron microscopy (HRTEM) with a field emission gun TECNAI G2 F20 microscope operated 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 by using EDX-mapping. In order to prepare the TEM samples, the powdered samples were treated by sonicating in absolute ethanol for several minutes, and a drop of the resulting suspension was deposited onto a holey carbon film supported on a copper grid, which was subsequently dried.

Catalyst 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. Temperature-programmed reduction (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 μ m 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 several sweeps up to a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 5 \times 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.³⁶ Atomic concentration percentages of the characteristic elements of the surfaces were

determined taking into account the corresponding area sensitivity factor for the different measured spectral regions.

Oxygen isotopic-exchange experiments were conducted using a quartz microreactor coupled to a quadrupole mass spectrometer (Omnistar, QMG 220 M1). Before each experiment the catalyst was initially pretreated at 450 °C for 2.5 h (in 50% $^{16}\text{O}_2/\text{Ar}$; flow 36 ml min^{-1}), followed by cooling down to 150 °C. Once achieved 150 °C, oxygen was replaced by argon (20 ml min^{-1}) and kept 1.5 h at that temperature before cooling down to 25 °C. For the temperature programmed isotopic exchange experiments (TPIE), the catalyst (0.160 g) was subjected to a 10% $^{18}\text{O}_2/\text{Ar}$ flow (22 ml min^{-1}) and the temperature was raised from 25 to 650 °C (heating rate of 10 °C min^{-1}). The concentration profiles of the exit gas composition were obtained by acquiring the mass spectra signals relative to $^{18}\text{O}_2$ ($m/e = 36$), $^{16}\text{O}^{18}\text{O}$ ($m/e = 34$) and $^{16}\text{O}_2$ ($m/e = 32$). Blank run experiments were performed using an empty reactor in order to check contributions of the gas-phase reactions, and stability of the mass spectrometer.

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 corresponds to a mixture consisting of $\text{C}_2/\text{O}_2/\text{He}$ with a molar ratio of 3/1/26. Typical reaction conditions used were 0.1 g of catalyst and 50 ml min^{-1} , although both the catalyst amounts loaded and the total flows used were largely varied 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 5A (2.5 m); and (ii) Porapak Q (3 m). Ethylene and carbon dioxide were the main

reaction products detected regardless of the catalysts tested. CO was also identified but generally with low selectivity. Blank runs in the absence of catalyst (also without CSi) showed no conversion in the range of reaction temperatures employed. Moreover, the carbon balance showed a high accuracy ($\pm 3\%$) in all the experiments undertaken

3. RESULTS AND DISCUSSION

3.1 Ethane ODH

A NiO supported on conventional silica (5 wt% NiO, named as **5NiSi** sample) was tested in the oxidative dehydrogenation of ethane, showing a low selectivity to ethylene (ca. 20%) (Figure 1A). In these experiments only two compounds were detected, ethylene and carbon dioxide, whereas not even traces of CO were observed. Interestingly, if represented the selectivity to ethylene with the ethane conversion at a fixed reaction temperature it can be observed that the selectivity to ethylene keeps rather unchanged (**5NiSi**, see Figure 1), demonstrating the low (or null) extent of the ethylene overoxidation in the range of conversions studied, which is related to the low capacity of nickel sites for ethylene decomposition. In fact, CO, which is not detected in this catalyst, is a reaction product mainly observed as a secondary product obtained from the deep oxidation of olefins.³⁷ It is noteworthy that **5NiSi** catalyst present a selectivity to ethylene lower than that of bulk NiO. Pure silica yields CO₂ as only reaction product in the oxidation of ethane (Table S1) but the catalytic activity is too low to be the origin of the lower selectivity of the NiSi catalyst. The dissimilar chemistry of bulk and supported NiO catalysts can be accounted for this result.

In order to improve the catalytic performance we decided to use pillared clay silica as a support for NiO instead of the conventional silica. This pillared clay presents a high surface area and therefore it likely leads to a better dispersion of nickel sites. In fact, it

has been recently reported that small NiO crystallites tend to produce more ethylene than large NiO crystallites.^{18,22} Then, for a proper comparison, two Ni loadings were chosen: i) low Ni-coverage (**5NiPCH** sample) with the same Ni-content than **5NiSi** catalyst and ii) higher nickel loading (**17NiPCH** sample) to ensure a similar surface coverage than **5NiSi** catalyst (see supporting information). A summary of catalytic results are presented in Table 1. As can be seen in Figure 1, for both catalysts synthesized with the pillared clay silica, the selectivity to ethylene highly increased (ca. 55-60%). As it happened with the reference silica-supported NiO (i.e **5NiSi**) catalyst, the selectivity to ethylene over PCH-supported nickel oxide catalysts remains almost constant in the ethane conversion range studied.

If compared the productivity to ethylene of the catalysts with a 5 wt.% of NiO (i.e. **5NiSi** and **5NiPCH**) it can be seen that the value for the catalyst supported on the pillared clay structure is ca. 5 times higher than that of the catalyst supported on the conventional silica (152.0 vs 27.3 g_{C₂H₄} kg_{cat}⁻¹ h⁻¹, respectively) (Table 1), and this is due not only to a remarkably higher selectivity to ethylene but also to a higher catalytic activity (Figure 1B).

Pillared clays can be synthesized using different components in the columns, although in many cases the structure collapses. Among the cations capable of forming the columns maintaining the structure we have selected TiO₂ as it presents rather acidic characteristics which have been reported to favor the ethylene production. The role of the acidic sites in the ODH of ethane has been described to be related to the ease for the ethylene desorption thus decreasing the ethylene overoxidation. However, in a recent paper these conclusions about the ethylene desorption were questioned^{19,22} although the positive role of the acid sites was also observed. Thus, pillared clays with Si/Ti pillars were used as supports for nickel oxide. As can be seen in Figure 1A the selectivity to

ethylene reached ca. 80% over **17Ni-PCH-Ti** catalyst. Again the value of the selectivity maintained in a similar level in the range of conversions studied.

Since NiO supported on Ti-containing clay demonstrated to be the most efficient system for ethane ODH, a wide range of Ni compositions were studied with this support (5, 10, 17, 50 and 80 wt. % of NiO). Table 1 shows comparatively the catalytic performance at 450 °C for the catalysts prepared in the present work, whereas Figure 2 shows the influence of NiO-loading in PCH-Ti catalysts on both the catalytic activity for ethane conversion and the selectivity to ethylene (at ethane isoconversion and isothermal conditions). At low nickel loading, i.e. **5NiPCH-Ti** and **10NiPCH-Ti**, the selectivity to ethylene exceeds 60% and increases with the nickel loading until a 17 wt% NiO loading, which presents the best value, 79%. Further nickel contents until 80 wt% NiO, led to a slight decrease of selectivity. At this point, we want to remark that the addition of only a 20 wt% of support, as in **80NiPCH-Ti**, means an outstanding improvement in the selectivity to ethylene. **Using the most selective catalyst, i.e. 17NiPCH-Ti sample, yield to ethylene of 34.7% was obtained (ethane conversion = 51.5 %, oxygen conversion = 76.2%, selectivity to ethylene = 67.3 %) at 450 °C using a contact time (W/F) of 12 g_{cat} h (mol_{C2})⁻¹ and increasing the amount of oxygen in the feed (C₂/O₂/He with a molar ratio of 3/3/24). Further modifications in the reaction conditions could mean a larger improvement in the yield to olefin using these catalysts.**

In the case of promoted NiO catalysts, it has been reported that only small amounts of modifiers are required to achieve the optimal performance^{21,27-30} in the ODH of ethane as an excess of promoters tend to decrease the selectivity to ethylene^{19,27}. However, in the present article we observe that the optimal performance is obtained by supported catalysts with a higher amount of support (83-50%) suggesting that the interaction Ni-support or Ni-promoter presents some differences

3.2 Catalyst Characterization

The role of the support has been demonstrated to be of paramount importance. Thus, according to the catalytic results obtained it can be concluded that conventional silica does not seem to be an appropriate support to achieve high yields to ethylene. The influence the support exerts on the catalytic active sites can be in part related to the size of the NiO crystallites that the support induces. Comparing the supports alone, conventional silica and PCH, the main differences between them are related to structure and the surface area, but not in the composition. Thus meanwhile one is amorphous with surface area lower than $200 \text{ m}^2\text{g}^{-1}$, the second one presents a pillared structure and a surface area of ca. $600 \text{ m}^2\text{g}^{-1}$. Then, it is expected that PCH disperses NiO better on its surface. In fact, this is what has been observed. According to the data obtained from XRD (supplementary information, Figure S1) the only observed crystalline phases containing nickel that has been detected in all catalysts is NiO (JCPDS: 78-0643), although depending on the sample wider or narrower peaks have been detected. Thus, applying the Scherrer equation, it has been determined that meanwhile in silica-supported NiO catalysts the mean size of NiO crystallites is ca. 13 nm (Table 1), for PCH- and PCH-Ti -supported NiO is ca. 7 nm and this very likely influences the catalytic performance.

For a more comprehensive knowledge about the influence of the 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. In general, as we can observe in high magnification TEM, all the samples present homogeneous and nearly spherical nanoparticles with sizes mainly ranging from 5 to 20 nm. An extremely low number of smaller (2-4 nm) particles is also observed in

most of the samples analyzed. The images obtained by TEM confirm the trend suggested by XRD. Thus, in the **5NiSi** sample the crystallite size ranges from 10 to 24 nm with a mean value of NiO grain size of ca. 14 nm which is higher than that with the same NiO-loading but with PCH- and PCH-Ti as support (6 to 15 nm with a mean value of ca. 9 nm).

In order to confirm the size and distribution of NiO nanoparticles, additional measurements in Dark field (DF-TEM) mode were made. Conventional DF-TEM imaging was achieved by selecting and inserting a small objective aperture around (111) and (002) diffraction spots from SAED pattern. Figure 4a shows an example of NiO nanoparticles in **17NiPCH** sample. As we can see in the dark field TEM micrograph the NiO nanoparticles are well dispersed with a size ranging from 6 to 18 nm and is matching with the data presented in Table 1. The circle in SAED pattern presents the position of objective aperture in DF mode.

On the other hand, it must also be confirmed that other Ni phases apart from NiO are not apparent in any of the catalysts studied. In this way SAED patterns were recorded and indexed from prepared samples. The concentric rings in the zero order Laue zone (ZOLZ) are produced by the small nanoparticles randomly orientated giving a continuous angular distribution of (hkl) spots at a distance $1/d_{hkl}$ from the (000) spot. SAED pattern showed at list 3 concentric rings formed by clear small spots (in some diffused rings); the samples consist of small crystalline nanoparticles of NiO. The measured interplanar distance from diffraction rings were about 0.24, 0.28 and 0.148 nm and could be, respectively, attributed to (111), (200) and (220) family plane of NiO. SAED patterns of NiO were indexed to Face-centered cubic phase structure space group Fm3m of NiO (JCPDS: 78-0643).

Figure 4b shows a high resolution TEM image of a NiO nanoparticle of ca. 10 nm in **17NiPCH-Ti** catalyst. The measured interplanar distance from the Fast Fourier Transform (FFT) pattern of the selected nanoparticle in HRTEM micrograph were about 0.24 nm and 0.28 nm corresponding to the (111) and (200) family plane respectively. The FFT pattern could be indexed to face centered cubic phase structure of NiO and is in good agreement with the results obtained by SAED and confirmed the nature of nickel oxide nanoparticles. In fact, as the control of the beam position and spot size is possible in our TEM microscope operating in nanoprobe mode, the chemical composition of selected areas of the samples was achieved. The comprehensive EDX analysis of the samples showed overall compositions similar to the theoretical ones. Fig. S2 (supplementary information) shows a representative EDX spectrum of a single NiO nanoparticle, in which Ni and O atoms are only detected apart from copper and carbon which has their origin in the copper grid employed.

The NiO crystallite sizes in catalysts of PCH-Ti-series are similar (or slightly smaller) than those of PCH-series and smaller than those on commercial silica. According to microscopy data, a parallelism between crystal size and selectivity to ethylene is not completely achieved, underlining that other aspects have to be considered. In this way, it is not wrong to consider that the reactivity of these catalysts can be also influenced by the presence of different crystal faces, i.e particle morphology, and by the presence of structural defects, grain boundaries, and/or surface dislocations. Indeed, previous literature data have shown how these parameters influence drastically the reactivity and the nature of active surface oxygen species in metal and metal oxides.³⁸

Modification in crystal face lattice parameters could give some indication 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. While the measured lattice parameter of the (200) and (220) crystal face changes in agreement with the crystal size, not such a trend is observed on the (111) crystal face (see [Table 2](#)). Surface dislocations or structural defects could explain this behavior, and has to be taken into account in order to explain the catalytic behavior of the studied catalysts.

Additional information about the electronic structure of NiO nanoparticles, can be obtained from the Ni $2p$ XPS data (included in Fig. 5 and [Table 3](#)).

The Ni $2p_{3/2}$ core level spectra of the studied catalysts (Fig. 6) show one main peak in the range 854.9-855.6 eV together with a satellite structure at higher BE, S(II) (~7eV of the main line). Moreover the line broadening of the main $2p_{3/2}$ line suggests the existence of another satellite, S(I), at ~1.5 eV higher BE of the main line. Peaks BE, relative intensities of both Ni $2p_{3/2}$ satellites and catalyst surface compositions are summarized in [Table 3](#). The relative intensity of the Ni $2p_{3/2}$ satellites to main peak have been reported to be related to the local environment and symmetry of the core hole site, surface and/or structural density of defect sites and their distribution, NiO particle size, as well as due to structural transitions.³⁸ In this sense, a detail analysis of the satellite structure could give very valuable information about the chemical structure of nanostructured nickel oxide particles, which should be related with catalytic properties. Interestingly, regardless of the support, the intensity ratio of S(II) to main peak correlates linearly with the selectivity to ethylene (Fig. 6a). Similar correlation has already been found over SnO₂- promoted NiO catalysts.²¹

Reducibility of this nickel based catalysts has been estimated through temperature programmed reduction experiments. [Table 3](#) summarizes the results for temperature programmed reduction experiments. As can be seen in Figure 7 there is a reduction band with high intensity at variable temperatures which depend on the catalyst and a

second band of lower intensity at higher temperatures. These bands have been related to the reduction of Ni^{2+} or Ni^{3+} to metallic nickel in different environments.^{39,40} Thus, catalysts supported on conventional silica present the highest reducibility (main bands at ca. 290 °C) whereas those supported on PCH-Si (main bands at 330-360°C) and especially on PCH-Ti (at 350-420 °C) present lower reducibility. The different reducibility of the NiO catalysts depending on the support can be tentatively explained on the basis of both the surface area and the nature of the support. The high surface area of PCH facilitates the dispersion of NiO on its surface, then forming smaller crystallites which are strongly bond to the support and consequently the reducibility is low. On conventional silica, which presents a lower surface area, the dispersion is worse and Ni species are not so strongly bond to the surface, thus presenting a higher reducibility. On the other hand, pure TiO_2 disperse metal oxides such as VO_x , NiO or MoO_x better than pure SiO_2 . Accordingly the replacement of part of the silica by titania in the PCH structure improves the NiO dispersion and decreases the reducibility.

Regardless of the support an inverse relationship can be clearly established between reducibility and selectivity to ethylene (Figure 6b), likely indicating that highly reducible nickel species tend to activate ethane in a non-selective way leading to the formation of carbon dioxide. In the NiPCH-Ti series it is observed that by increasing the nickel loading the reduction bands shift towards higher temperatures until 17NiPCH-Ti, which is the most selective catalyst. Further nickel loadings lead to a decreased reducibility, which agrees with a lower selectivity to ethylene. No correlation between NiO particle size and reducibility could be observed.

It is known that the amount and type of oxygen available in the catalysts is determinant for the catalytic activity and the selectivity in oxidation reactions. In this way $^{18}\text{O}_2$ isotopic-exchange experiments can be used to determine the reactivity of surface

oxygen.⁴¹ Thus depending on the relative rates of oxygen dissociation, surface exchange process, lattice incorporation, and diffusion into the bulk different concentrations of $^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ will be detected.^{42,43} The formation of $^{16}\text{O}^{18}\text{O}$ takes place if the oxygen dissociates fast and a rapid surface oxygen exchange process takes place compared with the oxygen diffusion rate in and from the bulk. On the other hand $^{16}\text{O}_2$ is predominantly formed when there is a fast incorporation reaction and subsequent diffusion step in and from the bulk.⁴⁴ Thus the release of $^{16}\text{O}^{18}\text{O}$ is associated with the presence of active electrophilic surface oxygen species (O^- , O_2^- , O_2^{2-}), whereas $^{16}\text{O}_2$ is associated with the presence of active lattice oxygen species. Figure 9 shows the isotopic oxygen exchange profile for NiO catalysts with different supports. Clear differences have been observed among them. The catalyst with SiO_2 as a support shows high activation ability for $^{16}\text{O}^{18}\text{O}$ formation, with an onset temperature of 377 °C whereas no release of $^{16}\text{O}_2$ was detected in the range of temperatures studied (Fig. 8) (and Table S2 in supporting information). For the catalysts with the PCH support the T_{onset} for $^{16}\text{O}^{18}\text{O}$ is higher, 425°C, and for the catalyst supported on PCH-Ti is the highest, 450°C. Conversely to 10NiSi, the catalysts supported on PCH and PCH-Ti show remarkable release of $^{16}\text{O}_2$, in both cases the T_{onset} being 419 °C. According to this, SiO_2 -supported NiO catalyst seems to stabilize a large amount of nonstoichiometric electrophilic oxygen species, which has been reported as non-selective,²² with practically no participation of lattice oxygen species.

However for the catalysts supported on PCH and especially the catalyst supported on PCH-Ti the contribution of lattice oxygen is remarkable (Figure 8) (Table S2). Figure 6c shows the relationship between the relative formation (until 650 °C) of $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}$ and the selectivity to ethylene (at isoconversion conditions) achieved. It can be seen a direct relationship in a way that the higher the proportion of $^{16}\text{O}_2$ released the higher is

the selectivity to ethylene. These results fit with the fact that the formation of ethylene from ethane on NiO-based catalysts proceeds through a MVK mechanism which involves the important contribution of lattice oxygen species. Accordingly, the catalysts most selective to ethylene show in TPIE experiments an important release of $^{16}\text{O}_2$ species and a lower reactivity toward $^{16}\text{O}^{18}\text{O}$ formation. Then the selective oxidation by redox mechanism is favored especially if the support is PCH-Ti. On the other hand the formation of CO_2 takes place mainly through the reaction of hydrocarbons with adsorbed electrophilic oxygen species.

3.3 General remarks

In view of our data, we can infer that large NiO particles as those in NiSi catalysts, favors the formation of highly reactive surface species which are selective towards the formation of CO_2 . **In fact, the selectivity observed over NiSi catalysts is similar to that reported previously for bulk NiO⁴² and even lower than that obtained for bulk NiO in the present article.** Conversely, the use of Porous Clay **Heterostructures** as supports for NiO leads to small NiO particles on which the formation of electrophilic oxygen species is delayed and the reactivity of lattice oxygen species is improved. However the particle size does not seem to be the only factor for obtaining high selectivity to olefins as catalysts supported over PCH-Ti form more ethylene than catalysts supported on the same structure but without Ti-atoms (Si-pillars) in spite of the fact that the crystallite size is similar for both series of catalysts. Moreover high Ni-loadings on PCH-Ti also lead to higher crystallite size but the high selectivity is kept. Factors like acidity should be taken into account but also other aspects; morphology of the NiO nanoparticles, crystal faces, surface and structural defects may play an important role on molecular oxygen activation and the reactivity of surface and/or lattice oxygen species, influencing

in such way the selectivity to products. Indeed, a dependence of the selectivity to ethylene with the chemical structure of the NiO nanoparticles has been deduced from the XPS data where a lineal correlation between the relative intensity of the Ni $2p_{3/2}$ satellite structure and the selectivity to ethylene has been observed (Fig. 6a). The intensity of the Ni $2p_{3/2}$ satellite structure is strongly influenced by the local environment of the Ni atoms, surface and structural defects and structural transformations. Moreover structural effects have been reported to influence oxygen activation and reactivity of oxygen species. **Indeed, by analyzing the NiO crystal structure of the most selective sample, a higher distortion of the crystal lattice (a-lattice parameter measured from (111) follows a different trend that if measured from (200) and (220) facets) could be detected,** and a higher contribution and reactivity of lattice oxygen species versus surface species as deduced from the TPIE data (Figure 6c). Accordingly a lower S(II) to main peak ratio in the Ni $2p_{3/2}$ XPS spectra has been evidenced.

On the other hand, a parallelism between the selectivity to ethylene and the lower reducibility of catalysts is also observed (Fig. 6b), which suggest that the higher the interaction of NiO particles with the support the higher is the selectivity to ethylene and probably the lower the reactivity of oxygen species.

Finally, we want to mention that the selectivity to ethylene obtained with Ni/PCH-Ti catalysts are similar (or slightly lower) that those reached by the most promising promoted NiO catalysts (Ni-Nb-O) but using higher reaction temperatures and lower oxygen concentration in the feed.^{31,42}

Conclusions

The use of Porous Clay Heterostructures as supports for nickel oxide in the oxidative dehydrogenation of ethane has been demonstrated to be a very interesting option. In fact

if these clays are used as support the selectivity towards ethylene is remarkably higher than if conventional silica is used. This improved performance has been associated to a higher dispersion of nickel oxide particles on the support that leads to a lower reducibility of the nickel. Thus, it seems that readily reducible nickel species detected by TPR favour the transformation of ethane into carbon dioxide. However the nickel oxide dispersion does not seem to fully determine the catalytic performance and other factors should be also considered. In this way, the particle morphology seems to play an important role on the catalyst selectivity since a higher distortion of the NiO crystal lattice parameter has been observed in the most selective catalysts and a correlation between extent of NiO distortion (see XPS and TEM) and selectivity to ethylene evidenced.

In accordance, the reactivity of lattice versus surface oxygen species is strongly influenced by the chemical structure of NiO nanoparticles evidencing a higher contribution of reactive lattice oxygen species (detected by isotopic $^{18}\text{O}_2$ exchange experiments) and a lower reactivity of surface oxygen species on the most active catalysts.

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