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Isotopic and *in situ* DRIFTS study of the CO₂ methanation mechanism using Ni/CeO₂ and Ni/Al₂O₃ catalysts.

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Graphical abstract

Highlights

- The CO₂ methanation mechanism has been studied for Ni/CeO₂ and Ni/Al₂O₃ catalysts
- Ni/CeO₂ present higher methanation activity and CH₄ selectivity than Ni/Al₂O₃
- Ni/CeO₂ combines two types of active sites efficient for CO₂ and for H₂ dissociation, respectively
- Specific active sites are not presented in Ni/Al₂O₃, all mechanism steps take place on the same active sites.
- Faster chemisorption and dissociation of CO₂ is allowed in Ni/CeO₂ surface
- Slow release of water and the accumulation of surface formates delay the further CO₂ chemisorption in Ni/Al₂O₃

Abstract

The CO₂ methanation mechanism was studied for Ni/CeO₂ and Ni/Al₂O₃ catalysts. The higher methanation activity and selectivity of Ni/CeO₂ is attributed to: i) Ni/CeO₂ combines two types of active sites efficient for CO₂ dissociation at the NiO-Ceria interface and for H₂ dissociation on Ni⁰ particles; ii) water desorption is the slowest mechanism step, and, due to the high oxygen mobility throughout the ceria lattice, water is not necessarily formed on the same active sites that chemisorb CO₂, i.e., the CO₂ chemisorption sites are not blocked by water molecules; iii) the Ni/CeO₂ surface does not accumulate carbon-containing species under reaction conditions, which allows faster chemisorption and dissociation of CO₂. The Ni/Al₂O₃ catalyst handicaps are that all the steps of the mechanism take place on the same active sites, and the slow release of water and the accumulation of surface formates on these sites delay the chemisorption of further CO₂ molecules.

Keywords: CO₂ methanation; nickel; ceria; metal-support interaction; mechanism; isotope.

1.- INTRODUCTION.

Substitution of fossil fuels by clean energy sources is one of the main worldwide challenges to face the problem of global warming. H₂ obtained by renewable energies will probably be an important energy vector in the future and for that reason, suitable H₂ storage and transportation technologies are being developed.

One of the options is CO₂ hydrogenation to yield CH₄, which is known as Sabatier's reaction or CO₂ methanation reaction [1,2]. CH₄ can be stored and transported more easily than H₂ using the already available infrastructures used for natural gas. In addition, this process contributes to mitigate the emission of CO₂ to the atmosphere if the energy used both for H₂ production and for acceleration of the Sabatier's reaction comes from renewable sources [3].

From a thermodynamic point of view the methanation reaction is exothermic, but kinetics at low temperature are not favorable because both CO₂ and H₂ molecules are quite stable and an important energy barrier must be overcome to break their bonds. In addition, the CO₂-H₂ reaction can yield different reaction products, such as CO, different hydrocarbons, alcohols, etc, and selectivity towards CH₄ is necessary in this case. Several catalysts have demonstrated to accelerate CO₂ and H₂ dissociation, and to favor the formation of methane as main reaction product. These catalysts include nickel [4–11] and novel metals (ruthenium [1,12–19], palladium [20–22] and rhodium [23–26], the former being a promising option for practical use due to the lower price.

Two reaction mechanisms have been proposed to describe the catalytic hydrogenation of CO₂ [27], the so-called associative mechanism and the dissociative mechanism. They mainly differ on the pathway for chemisorption and dissociation of the CO₂ molecules. In the associative mechanism, CO₂ is molecularly chemisorbed, and CO₂ oxygens are removed by H₂ afterwards in two consecutive steps. On the contrary, in the dissociative mechanism the CO₂ molecules dissociate upon chemisorption, yielding a surface carbonyl and an oxygen atom that reacts with H₂ afterwards.

The type of CO₂ methanation mechanism depends on the catalyst, and understanding the reaction pathways taking place is necessary for further design better catalysts. It has been reported [28] that CeO₂-supported Ni catalysts are more active and selective towards CH₄ formation than Ni catalysts supported on Al₂O₃, TiO₂ and MgO, but the mechanisms responsible of these differences have not been studied in detail. Also, Ni/Ce_{0.5}Zr_{0.5}O₂ has been reported [7] to be more active than Ni/γ-Al₂O₃, and differences in the type of surface CO₂ species were detected upon CO₂ chemisorption in the absence of H₂.

The goal of this article is to study differences in the role of the CeO₂ and Al₂O₃ supports in the Ni-catalyzed CO₂ methanation reaction, and isotopic C¹⁸O₂ experiments and in situ DRIFTS reactions have been carried out for this purpose.

2.- EXPERIMENTAL DETAILS.

2.1. Catalysts preparation.

Two catalysts have been prepared and used in this study, which are referred as Ni/CeO₂ and Ni/Al₂O₃. Commercial γ-Al₂O₃ was supplied by Alfa Aesar (Stock nº 43855) and CeO₂ was prepared by calcination of cerium citrate at 600 °C for 6 hours. Cerium citrate was prepared by precipitation using an ethanolic solution of Ce(NO₃)₃·6H₂O (99.5%, Alfa Aesar) and citric acid (99%, Sigma-Aldrich) in stoichiometric proportions. Nickel was loaded by incipient wetness impregnation using a Ni(NO₃)₂·6H₂O (Sigma-Aldrich) ethanolic solution. The catalysts were calcined at 600 °C in static air for 6 hour using a heating rate of 5 °C/min. The target Ni content was 8.5 w/w %.

2.2. Catalysts characterization.

The nickel content was determined by ICP-OES after the catalyst were completely dissolved in a HCl + HNO₃ mixture (3:1 in volume), being assisted by microwaves.

X-ray diffractograms were obtained in a Rigaku Miniflex II diffractometer using CuK_α radiation ($\lambda = 0.155418$ nm) between 10° and 90° 2 θ angles, with a step of 0.025°.

N₂ adsorption-desorption isotherms were measured at -196 °C in an Autosorb-6 device, from Quantachrome, after outgassing the catalysts under vacuum at 150 °C for 2 h.

H₂-TPR characterization was carried out in a Micromeritics Pulse ChemiSorb 2705 device, using 40 ml/min of 5% H₂/Ar flow. 40 mg of catalyst were loaded on a tubular quartz reactor coupled to a TCD detector, and the temperature was raised from room temperature to 950 °C at 10 °C/min.

X-ray photoelectron spectroscopy (XPS) characterization was carried out in a K-ALPHA Thermo Scientific device (Al-K α radiation; 1486.6 eV), using an X-ray spot with 400 μ m diameter, 3 mA and 12 kV. The binding energy scale was calibrated by setting the C1s peak at 284.6 eV. Ce3d, O1s, and Al2p spectral regions were scanned several times to obtain good signal-to-noise ratios. The spectra obtained after background signal correction (Shirley-type background) were fitted to Lorentzian and Gaussian curves in order to obtain the number of components, the position of each peak, and the peak areas. XPS characterization was made to both the pre-treated and used catalysts.

2.3. Catalytic tests.

Catalytic tests were performed in a fixed-bed 9 mm inner diameter cylindrical reactor using 400 mg of catalyst mixed with quartz particles (1-1.25 mm). The bed

volume was 1 cm³ and the GHSV was 12000 h⁻¹. The gas composition was monitored with a gas chromatograph (Agilent HP7890B). The catalyst was pre-treated at 500 °C for 1 hour under 20% H₂/He (200 cm³ min⁻¹), and after cooling to 200 °C in inert gas, the reaction mixture (16 % CO₂ + 64 % H₂ and He balance) was fed with a total flowrate of 200 ml/min. The temperature was raised to 450 °C in steps of 25 °C, with a heating rate of 5 °C/min between steps, and the gas composition was measured in each step under steady state conditions.

2.4. Isotopic experiments.

Isotopic experiments were carried out with ¹³C¹⁸O₂ (Aldrich; 99% ¹³C, 95% ¹⁸O) pulses, in a cylindrical reactor (inner diameter 4 mm) coupled to a mass spectrometer Pfeiffer Vacuum (model OmniStar) operating at 1 second frequency. The catalyst (50 mg) was pretreated in 50 % H₂/He (20 ml/min) at 500 °C for 60 minutes, and then the temperature was stabilized at 350 °C under the same gas flow, which was kept for the whole experiment. A six-way valve with a loop of 100 µl was used, which was filled at 9 psi with the gas to be pulsed. This volume of gas is dragged by the main gas stream once the position of the valve is changed. Three Ar pulses were first fed, and afterwards, three pulses of ¹²C¹⁶O₂ followed by three pulses of ¹³C¹⁸O₂. The pulses were fed in intervals of 7 minutes, which allows stabilization of all m/z signals after the previous pulse.

2.5. *In situ* DRIFTS experiments.

In situ DRIFTS experiments were performed in an infrared spectrometer Jasco, model FT/IR-4100 using a reaction cell for temperature and reaction gas control. The cell was designed to allow the gas flow through the catalytic bed (70 mg of undiluted catalyst). The catalyst was pretreated in 50% H₂/He at 450 °C for 60 minutes, and then was cooled down to room temperature under H₂/He mixture. The background spectrum was recorded in He, and then, the methanation mixture (16 % CO₂ + 64 % H₂ and He

balance) was fed and the temperature was raised up to 450 °C in steps of 50 °C. Spectra were recorded after 60 minutes in isothermal conditions at each temperature from 4000 to 1000 cm⁻¹ with a step of 1 cm⁻¹.

3.- RESULTS AND DISCUSSION.

3.1. Catalysts characterization by N₂ adsorption, XRD and H₂-TPR.

Figure 1 shows the N₂ adsorption-desorption isotherms recorded at -196°C, and the BET specific surface areas determined from these isotherms are included in Table 1.

Figure 1. N₂ adsorption-desorption isotherms at -196 °C.

Table 1. Results of the catalysts characterization by ICP and N₂ adsorption.

	Ni (wt. %)	BET specific surface area (m ² /g)
Ni/Al ₂ O ₃	9.4	172
Ni/CeO ₂	8.2	10

N₂ uptake is significantly higher for Ni/Al₂O₃ than for Ni/CeO₂, which is consistent with the BET values (172 vs 10 m²/g, respectively). The shape of the Ni/Al₂O₃ isotherm combines rapid N₂ uptake at very low relative pressure, which could be related with the presence of micropores, with smooth uptake at intermediate pressures and a hysteresis loop above $P/P_0 = 0.5$ that evidences the presence of mesopores. This type of porosity is characteristic of the commercial γ -Al₂O₃ support used in the preparation of this catalyst. The low porosity of the Ni/CeO₂ catalyst is also expected due to CeO₂ support being prepared by calcination of citrates.

The crystalline phases were studied by XRD, and the diffractograms of the two catalysts are included in Figure 2.

Figure 2. X-Ray diffractograms of the catalysts.

The Ni/CeO₂ catalyst shows peaks attributed to CeO₂ (JCPDS 00-034-0394) and NiO (JCPDS 01-075-0269) [29,30], and the Ni/Al₂O₃ catalyst shows peaks of the γ -Al₂O₃ phase [31]. CeO₂ crystallizes in fluorite structure, with main peaks at 28.5, 33.1, 47.6, and 56.5°, and these peaks are sharper than those of the γ -Al₂O₃ phase. The broad peaks of γ -Al₂O₃ are consistent with the low crystallinity of this phase. The tiny peaks of the cubic structure of NiO at 37.5, 43.4 and 63.0° are properly identified in the Ni/CeO₂ diffractogram, but are not so obvious in that of Ni/Al₂O₃. This is, in part, because some NiO and γ -Al₂O₃ peaks appear at similar angles, and the broad γ -Al₂O₃ peaks mask the tiny peaks of NiO. However, the intensity of the (200) NiO peak at 43.4°, which is observed in both diffractograms, is much better defined in that of Ni/CeO₂, and this suggests that NiO crystals are smaller on Ni/Al₂O₃ than on Ni/CeO₂. Quantitative comparison of the NiO crystallite sizes is not possible because the crystallite size cannot be obtained for Ni/Al₂O₃. The smaller crystals of NiO on γ -Al₂O₃ can be attributed to the better dispersion due to higher surface area of the γ -Al₂O₃ support with regard to CeO₂.

The redox properties of the catalysts was studied by H₂-TPR experiments, and the reduction profiles are shown in Figure 3. Reduction of the Ni/CeO₂ catalyst takes place at much lower temperature than Ni/Al₂O₃ reduction, as expected, showing several reduction events. On the one hand, a small sharp peak is observed at 250 °C, with small shoulders at lower temperature that can be assigned to NiO reduction [28]. The amount of H₂ consumed has been calculated and it is estimated that only 1.6 % of the total amount of NiO loaded on the catalyst has been reduced in this event. On the other hand, a large peak appears at 345 °C with a shoulder at higher temperature, corresponding the amount of H₂ consumed to a 122% of NiO available, i.e., not only NiO is being reduced in this event but also part of surface CeO₂. Moreover, a third peak is observed at 810 °C related to the reduction of bulk ceria.

In the case of Ni/Al₂O₃ catalyst, the reduction starts at 500 °C and a main peak is observed at 825°C with two shoulders at 725 and 600 °C. The total amount of H₂ consumed is that required for 100% NiO reduction to Ni⁰. Al₂O₃-supported NiO has been reported to be reduced in three events [32,33], which is consistent with the shape of the Ni/Al₂O₃ reduction curve shown in Figure 3. The low temperature shoulders are attributed to reduction of NiO species with different interaction with alumina, the interaction being weaker for 600 °C-reduced species and stronger for those reduced at 725 °C [34,35]. Finally, the highest temperature peak at 825 °C is assigned to well dispersed NiAl₂O₄ spinel reduction.

Figure 3. H₂-TPR characterization of the catalysts

In conclusion, characterization results evidence that the γ -Al₂O₃ support has much higher surface area than ceria, and NiO seems to be better dispersed on the alumina support than on ceria. However, NiO reduction is improved in the Ni/CeO₂ catalyst with regard to Ni/Al₂O₃, with evidences a simultaneous reduction of NiO and surface CeO₂.

3.2. Catalytic tests.

The catalytic methanation of CO₂ has been studied, and the CO₂ conversion curves are shown in Figure 4a together with CH₄ selectivity profiles in Figure 4b.

Figure 4. CO₂ methanation catalytic tests. (a) CO₂ conversion and (b) CH₄ selectivity.

The Ni/CeO₂ catalyst is much more active than Ni/Al₂O₃, with onset CO₂ conversion at 250°C and a progressive increase until reaching the equilibrium curve at 375°C. CH₄ is the only reaction product, with 100% selectivity in the whole range of temperatures screened.

The catalytic activity of Ni/Al₂O₃ is much lower, with a slow increase in CO₂ conversion above 250 °C and without reaching thermodynamic equilibrium conversions in the range of temperatures studied. The CH₄ selectivity is not 100% in this case and CO is also produced together with CH₄, the CH₄ selectivity increasing with temperature from 65 to 90%.

These differences in catalytic activity have been already reported by other authors [7,28], and the higher activity and selectivity of ceria-supported nickel catalysts with regard to Ni/Al₂O₃ has been tentatively attributed to differences in the reaction intermediates created upon CO₂ chemisorption and to the reducibility of ceria. XPS characterization, isotopic experiments and catalytic reactions followed by in situ DRIFTS have been carried out in this study, and results are discussed in the coming sections providing further insights about the role of the support in the Ni-catalysed CO₂ methanation.

3.3. Fresh and used catalysts characterization by XPS.

Changes in the oxidation state of nickel during the catalytic tests were studied by XPS by analyzing the Ni2p energy region for both catalysts before and after the catalytic experiments. Figure 5 compiles the spectra, where important differences are noticed depending on the catalyst support.

Figure 5. a) Ni2p spectra b) Ce3d and Al2p and c) O1s of the catalysts before and after the catalytic tests.

Ni2p spectra can be deconvoluted in several contributions, but there is not a general consensus about the assignation of these bands. It has been suggested that the

position of the most intense peak can be used to determine the oxidation state of nickel and to obtain information about the charge density of its cations [36–39]. According to literature, the main peaks centered at 852.3, 853.4 and 856.7 eV can be assigned to metallic Ni, NiO, and Ni₂O₃, respectively [40–43]. The peak at 856.0 eV can be also attributed to surface Ni³⁺ species associated to the presence of Ni²⁺ vacancies in NiO crystal lattices [34], which is close to the binding energy of Ni₂O₃ and Ni(OH)₂ [44].

The main peak for the Ni/Al₂O₃ catalyst is centered at 855.9 eV, and this energy is consistent with the presence of Ni²⁺ cations, either forming NiO or partially hydrated oxides [37,38,45]. The Ni2p spectrum of Ni/Al₂O₃ does not change during the catalytic tests, suggesting that the charge density of the Ni²⁺ cations is the same before and after methanation.

However, the main Ni2p peak for the Ni/CeO₂ catalyst is centered at 854.8 eV, that is, there is a shift of more than 1 eV in the binding energy of this main peak with regard to Ni/Al₂O₃, and this is an evidence of the different NiO-support interaction. The main peak in the Ni2p spectra of Ni/CeO₂ also shows a shoulder at low binding energy (852.2 eV), which indicates the presence of Ni⁰. The coexistence of these two nickel species is very positive for the CO₂ methanation reaction, because nickel oxide species in close contact with ceria are active sites for CO₂ chemisorption and dissociation, and Ni⁰ species are effective sites for H₂ dissociation [46]. This distribution of nickel species, combining Ni²⁺ and Ni⁰, is maintained after the catalytic tests, and this is consistent with the stability of this catalyst previously demonstrated in 24 hours stability tests [47].

Ce3d and Al2p regions are depicted in Figure 5b. The Ce3d spectrum consists of 5 doublets (3d_{5/2} and 3d_{3/2} components), three of which correspond to Ce⁴⁺ (882.1–900.8 eV, 888.6–906.9 eV and 898.0–916.3 eV), while the remaining two are attributed to Ce³⁺ (880.6–898.9 eV and 883.9–902.0 eV). In turn, the peaks at 74.0 and 75.0 eV in Al2p region of Ni/Al₂O₃ catalyst indicates the presence of Al–O and Al–OH bonds,

respectively [48]. The distribution of Ce3d and Al2p species is maintained after the catalytic tests.

O1s region was also analyzed and results are collected in Figure 5b. Three peaks were required to fit this region for CeO₂-based catalysts centered at 529.0, 531.0 and 533.0 eV which can be assigned to lattice oxygen, surface-adsorbed oxygen, hydroxyl groups and carbonates, and molecular water, respectively [49,50] whereas two peaks localized at 531.0 and 532.3 eV are required for Al₂O₃-based catalysts which corresponds to Al–O and Al–OH, respectively [51,52]. This distribution of species, is maintained after the catalytic tests for Ni/Al₂O₃ catalyst, however for Ni/CeO₂ catalyst the relative concentration of surface-adsorbed oxygen, hydroxyl groups, carbonates, and molecular water decreases from 35.5 to 28.7 % which can indicate a removal of surface groups during the catalytic tests. To corroborate this, C1s region (region not shown) was also analyzed. It is observed that carbonates content decreases from 12.0 to 6.9 % after the reaction in Ni/CeO₂ samples whereas in Ni/Al₂O₃ this content does not decrease, even slightly increases from 7.5 to 8.4 %. This seems to indicate that whereas in Ni/Al₂O₃ catalyst carbon species are formed on the catalyst surface during the catalyst tests, in Ni/CeO₂ catalyst carbon species are removed from the catalyst surface.

3.3. Isotopic experiments.

The CO₂ methanation mechanisms have been studied for Ni/Al₂O₃ and Ni/CeO₂, and isotopic experiments have been performed with ¹³C¹⁸O₂ pulses in order to understand the role of catalyst oxygen during the reactions. Figure 6 shows results of the first ¹³C¹⁸O₂ pulse performed after a reference Ar pulse for Ni/Al₂O₃ (Figure 6a) and Ni/CeO₂ (Figure 6b). For proper interpretation of the results, note that not all m/z signals monitored during the experiments are plotted in these figures, i.e., those signals with negligible values are not included in Figure 6 for the sake of simplicity.

Figure 6. First pulse of Ar and $^{13}\text{C}^{18}\text{O}_2$ into a continuous flow of H_2 (50 % H_2 in He) at 350 °C over (a) $\text{Ni}/\text{Al}_2\text{O}_3$ and (b) Ni/CeO_2

The shape of Ar profile is characteristic of an inert gas pulse. Most signals detected once $^{13}\text{C}^{18}\text{O}_2$ is pulsed appear at the same relative time than Ar, considering time = 0 seconds the injection of the gas. These signals include CO_2 , CO and CH_4

species, which indicates that exchange of oxygens between CO₂ molecules and catalysts, all reaction steps required to hydrogenate CO₂, and the desorption of CH₄ and CO occur in a time frame much lower than the seconds scale of the measurements. The main difference between the Ar peaks and peaks of CO₂, CO and CH₄ species is the area, which is lower for reactants and products than for Ar, because they are affected by the reaction conversion. Only the H₂O signals appear delayed by 40-50 seconds with regard to the Ar reference, and this evidences that the H₂O desorption is significantly slower than the remaining steps of the mechanism. Note that CO is detected in the isotopic experiments but not in the catalytic tests performed with Ni/CeO₂, because the experimental conditions of both types of experiments are very different with much higher concentration of CO₂ in the catalytic tests than in the isotopic experiments.

¹³C¹⁸O₂ is not detected in the pulse experiments shown in Figure 6, and all oxygen-containing gases measured come with ¹⁶O of the catalysts. The detection of a high ¹³C¹⁶O₂ signal indicates that the double exchange of oxygen atoms between the ¹³C¹⁸O₂ pulsed and the catalysts takes place in a significant extent. ¹³C¹⁶O is also detected, probably because the catalysts are partially reduced by H₂ before the pulse, and part of the oxygens of ¹³C¹⁸O₂ reoxidise the catalysts. The release of ¹²C¹⁶O and ¹²CH₄, with ¹²C, evidences that surface carbon species chemisorbed on the catalysts before the ¹³C¹⁸O₂ pulse are also desorbed and participate in the hydrogenation processes.

For a quantitative analysis of the pulse experiments, the area of the different peaks has been calculated and expressed as mass balance. Figure 7 compiles the mass balances of carbon species, including CO₂, CO and CH₄ species, both with ¹²C and ¹³C, for the three consecutive ¹³C¹⁸O₂ pulses performed to each catalyst.

Figure 7. Percentage of carbon species in three consecutive pulses of $^{13}\text{C}^{18}\text{O}_2$ into a continuous flow of H_2 (50 % H_2 in He) at 350 °C over (a) $\text{Ni}/\text{Al}_2\text{O}_3$ and (b) Ni/CeO_2 .

The carbon species distribution keeps constant for the three pulses fed to Ni/CeO_2 , but not for those fed to $\text{Ni}/\text{Al}_2\text{O}_3$. The release of ^{18}O -containing species is almost

negligible for Ni/CeO₂ (only few ¹³C¹⁶O¹⁸O is detected), while for Ni/Al₂O₃, the ¹³C¹⁶O¹⁸O signal increases progressively at expense of the ¹³C¹⁶O₂ decrease. This means that both catalysts exchange oxygen with the CO₂ molecules, but the exchange capacity of ceria is much higher than that of alumina, as expected. This effect is also observed in the H₂O yielded as reaction product, as observed in the mass balances of H₂O plotted in Figure S1. Only H₂¹⁶O (98%) is detected for the three pulses carried out with Ni/CeO₂, while some H₂¹⁸O (11%) is observed in the third pulse to Ni/Al₂O₃.

As shown in Figure 7, the value of the sum of all CO₂ species is constant in progressive pulses for both catalysts, indicating that the conversions are always the same, and Ni/CeO₂ reaches higher conversions (lower $\sum$ CO₂ values) than Ni/Al₂O₃ in agreement with the catalytic tests.

The total amount of CH₄ (¹²CH₄ + ¹³CH₄) yielded as hydrogenation product is higher for Ni/CeO₂ than for Ni/Al₂O₃, which is also in accordance with the higher catalytic activity observed in the catalytic test results. Note that the percentages of ¹²CH₄ and ¹³CH₄ released are equal for Ni/CeO₂ and almost equal for Ni/Al₂O₃, and this evidences the hydrogenation of carbon species (with ¹²C) present on the catalysts before the ¹³C¹⁸O₂ pulses together with those created upon ¹³C¹⁸O₂ chemisorption.

¹³C¹⁶O and ¹²C¹⁶O signals are also observed for both catalysts. This was expected for Ni/Al₂O₃, because CO was also detected in the catalytic tests, but not for Ni/CeO₂. This apparent discrepancy between the catalytic tests and the isotopic experiments is attributed to the different experimental conditions used, CO₂ and H₂ being in stoichiometric conditions in the catalytic experiments but not in the pulse experiments with isotopic gas.

These isotopic experiments provide valuable information about the CO₂ methanation mechanism. It can be concluded that, in a first step, the CO₂ molecules are chemisorbed on the catalysts and, in most cases, the double C=O bonds are broken. This involves reduced sites of the catalyst that gets oxidized by CO₂. Then, different

reaction pathways can be followed. Part of the oxygens removed upon the double bonds breaking are replaced by catalyst oxygen and are released as CO or CO₂, leaving reduced sites on the catalyst again. Simultaneously, part of the carbon species adsorbed on the catalysts surface are hydrogenated and released as CH₄. Ni/CeO₂ is get involved very efficiently in these processes, and isotopic experiments suggest that the energy demanding dissociation of the CO₂ double bonds is significantly improved by this catalyst. As observed by XPS, the Ni/CeO₂ catalyst combines reduced nickel with cationic nickel species, and it is postulated that the cationic species are probably stabilized at the NiO-CeO₂ interface while nickel with poor contact with ceria is reduced more easily. This combines partially reduced nickel oxide actives sites for CO₂ dissociation in an oxidized environment located at the NiO-CeO₂ interface, with highly reduced nickel sites suitable for H₂ dissociation. Once ¹³C¹⁸O₂ is chemisorbed and dissociated at the NiO-CeO₂ interface, the adsorbed ¹⁸O are not necessary removed by H₂ in this particular active site. Probably, these oxygens are transferred to ceria using the oxygen vacancies created on this support through ceria oxygen removal by H₂ (yielding H₂¹⁶O) somewhere else on the ceria surface. That is why ¹⁸O is not detected in the isotopic experiments with Ni/CeO₂, because the ¹⁸O atoms left by ¹³C¹⁸O₂ are sent and get lost into the ceria support. This is possible due to the high oxygen and vacants mobility of ceria, while other metal oxides, such as alumina, do not have this option.

Ni/Al₂O₃ is also able to promote the dissociation of CO₂, which is evidenced by the detection of ¹³C¹⁶O₂ molecules (with catalyst oxygen), but Ni/Al₂O₃ is not as efficient as Ni/CeO₂. The detection of gas products with ¹⁸O after the first pulse of ¹³C¹⁸O₂ indicates that a high proportion of catalyst sites available for the dissociation of ¹³C¹⁸O₂ are used in the first pulse. These results also show that the ¹⁸O adsorbed in the first pulse is either removed by H₂, yielding H₂¹⁸O, or used in a further pulse to be exchanged with other ¹³C¹⁸O₂ molecule. One of the reasons of the lower activity of Ni/Al₂O₃ with regard to Ni/CeO₂ is that CO₂ dissociation and H₂O formation takes place in the same active

sites. As deduced from the shape of the H₂O peaks in the pulse experiments, H₂O desorption is much slower than CO₂ chemisorption and dissociation, and therefore, the slow desorption of H₂O limits further chemisorption and dissociation of other CO₂ molecules. On the contrary, the high oxygen mobility of oxygen into the ceria support allows dissociate CO₂ in certain active sites (probably at the NiO-CeO₂ interface) while H₂O is being formed and released somewhere else of the ceria surface.

3.4. *In situ* DRIFTS experiments.

In situ DRIFTS experiments were carried out to monitor the nature of the surface species present on the catalysts under reaction conditions at different temperatures, and Figure 8 compiles the recorded spectra.

Figure 8. In situ DRIFTS experiments under $\text{H}_2/\text{CO}_2/\text{He}$ at different temperatures. (a) $\text{Ni}/\text{Al}_2\text{O}_3$ and (b) Ni/CeO_2 . Spectra were recorded after 60 min under reaction conditions at each temperature and a background spectrum recorded at room temperature under He was subtracted in all cases.

Gas phase CO_2 provides an intense double band at 2350 cm^{-1} together with two double bands localized between 3500-3750 cm^{-1} . For easy identification of the surface

species on the spectra, Figure 9 shows a scheme of the main surface carbon species together with the ranges of wavenumbers active in infrared [21,46,53–57].

Figure 9. Scheme of surface carbon species and adsorption regions in infrared spectra.

Important information about the methanation mechanism is obtained from bands below 1700 cm⁻¹, and the behavior of these bands with temperature is different for Ni/Al₂O₃ (Figure 8a) and Ni/CeO₂ (Figure 8b).

The methanation reaction does not occur at 150 °C (see Figure 4), and the positive bands in the spectra of both catalysts evidence accumulation of surface species at this temperature. Ni/Al₂O₃ spectrum at 150 °C shows bands at 1652, 1430 and 1225 cm⁻¹ that can be assigned to bicarbonates, which are created by CO₂ chemisorption on hydroxyl groups. The O-H stretching of these bicarbonates is also observed at 3625 cm⁻¹. The role of the alumina support in the chemisorption of CO₂ was already described by other authors, this step playing an important role in the methanation reaction [5].

According to the catalytic tests (Figure 4), the onset reaction temperature is around 250 °C, and the Ni/Al₂O₃ spectra at this and higher temperatures evidence the depletion of bicarbonates and the formation of formates as reaction intermediates. The tiny bands at 3000 and 2900 cm⁻¹ are related to the C-H stretching mode of formates,

and the bands at 1588 and 1375 cm^{-1} correspond to their symmetric and asymmetric vOCO modes. The formation of formates upon CO_2 chemisorption, probably on hydroxyl groups of aluminina, is consistent with kinetic studies reported by other authors [8,58] predicting that CO_2 chemisorption on $\text{Ni}/\text{Al}_2\text{O}_3$ takes place with dissociation of one of the oxygens. The presence of formates under reaction conditions explains the production of CO during the catalytic tests. Formates are created once CO_2 is chemisorbed and partially hydrogenated, and these formates can be further hydrogenated yielding CH_4 or desorbed yielding $\text{CO} + \text{H}_2\text{O}$.

On the contrary, the behavior of Ni/CeO_2 is different. The spectrum of this catalyst at 150 $^\circ\text{C}$ shows bands at 1583 and 1297 cm^{-1} , which are consistent with the presence of bidentate carbonates in chelate configuration, and these bands disappear under reaction conditions. These two bands are negative at 250 $^\circ\text{C}$ and higher temperatures, which evidences the depletion of carbonates that were present on the samples when the background spectrum was recorded in He at room temperature. A small band is also observed at 1390 cm^{-1} at 150 $^\circ\text{C}$, and also disappears at higher temperatures. This band can be assigned to monodentate carbonates, and these species should additionally present bands around 1300-1370 cm^{-1} and 1040-1080 cm^{-1} which are hardly observed in Figure 8b. The absence of surface carbon species on the Ni/CeO_2 catalyst under methanation reaction conditions is consistent with the conclusions of the isotopic exchange experiments and XPS, that is, CO_2 is chemisorbed and dissociated on reduced sites of the catalyst and carbon intermediates are not observed by infrared because the carbon left is either desorbed as CO_2 taking oxygens from the catalyst or is hydrogenated yielding CH_4 .

3.5. $\text{CO}_2 + \text{H}_2$ reaction mechanism on Ni/CeO_2 and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts.

As a summary of the conclusions obtained by the different techniques used in this study, Figure 10 shows schemes with our outlook about the main steps of the CO₂ + H₂ reaction mechanisms taking place on Ni/Al₂O₃ and Ni/CeO₂.

Figure 10. Scheme of the CO₂ + H₂ reaction mechanisms on Ni/CeO₂ and Ni/Al₂O₃ catalysts.

The Ni/CeO₂-catalysed CO₂ methanation reaction starts with the reduction of the catalyst. This reduction takes place both at the NiO-CeO₂ interface, creating reduced sites on an oxidized NiO-rich environment, and on the ceria support creating oxygen vacancies. Among these sites, the NiO-CeO₂ interface is reduced more easily, but the ceria support is much more abundant, and therefore is statistically more accessible to H₂. Additionally, XPS results evidence that part of the NiO particles, those with poor interaction with the ceria support, are reduced to metal nickel where H₂ molecules are efficiently dissociated. CO₂ chemisorption takes place on the partially reduced NiO-CeO₂ interface, where CO₂ is dissociated, and oxygens are transferred to the ceria support to restore the oxygen balance. These oxygens move throughout the ceria lattice using the previously created vacancies. This transfer of oxygen from the NiO-CeO₂ interface to somewhere else into the ceria support leaves the active sites at the NiO-CeO₂ interface available for further CO₂ chemisorption. Hence, the H₂ reduction of the NiO-CeO₂ interface is not necessary after the chemisorption of every CO₂ molecule since the high oxygen mobility on this catalyst allows the reduction to take place somewhere else on the ceria surface. Isotopic experiments indicate that, upon CO₂ dissociation, the carbon atom either can accept ceria oxygens to yield CO₂ again or dissociated hydrogens to yield methane.

This mechanism is very effective for several reasons: i) the Ni/CeO₂ catalyst combines two types of active sites efficient for CO₂ and H₂ dissociation, respectively; ii) water desorption is the slowest step of the mechanism, as observed in the isotopic experiments and this product is not necessarily formed on the same active sites over which CO₂ is chemisorbed, i.e., the CO₂ chemisorption sites at the NiO-CeO₂ interface are not blocked by water molecules; iii) the catalyst surface does not accumulate carbon-containing species under reaction conditions, which allows faster chemisorption of CO₂.

The Ni/Al₂O₃-catalysed CO₂-H₂ reaction follows a different mechanism, and in this case, the participation of the alumina support is not so relevant. Hydroxyl groups are

created by H₂ reduction of the NiO–Al₂O₃ interface, where CO₂ is chemisorbed afterwards. The isotopic experiments indicate that part of the chemisorbed CO₂ molecules are desorbed after the CO₂ oxygens are exchanged by catalyst oxygens. In this case, unlike Ni/CeO₂, CO₂ oxygens cannot migrate throughout the alumina surface and remain wherever CO₂ has been dissociated. These chemisorbed CO₂ molecules block the active sites and hinder further CO₂ molecules chemisorption and dissociation. The CO₂ molecules that are not desorbed yield formates and water upon H₂ reduction, and these formates can react in two ways. Part of these formates are further hydrogenated yielding CH₄ + H₂O and part decompose yielding CO + H₂O, which explains the lower selectivity of Ni/Al₂O₃ observed in the catalytic tests. The handicaps of this reaction mechanism, in comparison to that taking place on Ni/CeO₂ are: i) There are not specific active sites for H₂ dissociation, and molecular H₂ must reduce surface species; ii) all the steps of the mechanism take place on the same active sites, and the slow release of water and the accumulation of surface formates on these sites delay the chemisorption of further CO₂ molecules.

4.- CONCLUSIONS.

The CO₂ methanation reaction mechanism has been studied for Ni/CeO₂ and Ni/Al₂O₃ catalysts, and the following conclusions can be summarized:

For both catalysts, isotopic experiments evidence a dynamic equilibrium between gas phase CO₂ and catalyst oxygen, consisting of CO₂ chemisorption, exchange of CO₂ oxygens with the catalysts, and CO₂ desorption. In the presence of H₂, part of the chemisorbed CO₂ is desorbed after oxygens exchange and part is hydrogenated.

The higher methanation activity and 100% CH₄ selectivity of Ni/CeO₂ is attributed to the following mechanistic aspects: i) the presence of two different active sites for the CO₂ dissociation (NiO–Ceria interface) and for H₂ dissociation (reduced Ni⁰ particles)

which was pointed out by XPS; ii) pulse experiments indicate that the slowest step of the mechanism is the water desorption, however, in Ni/CeO₂ catalysts due to the presence of two type of active sites and the high oxygen mobility throughout the ceria lattice, the formation of water not necessarily occurs in the CO₂ chemisorption sites and thus the NiO-CeO₂ interface are not blocked by water molecules; iii) faster chemisorption and dissociation of CO₂ is allowed in Ni/CeO₂ surface due to the not accumulation of carbon-containing species under reaction conditions as was observed by in situ DRIFTS experiments.

The handicaps of the Ni/Al₂O₃ catalyst, in comparison to Ni/CeO₂, are: i) There are not specific active sites for H₂ dissociation, and molecular H₂ must reduce surface species; ii) all the steps of the mechanism take place on the same active sites, and the slow release of water and the accumulation of surface formates on these sites delay the chemisorption of further CO₂ molecules. The formation of formates as reaction intermediates results in the production of CO as undesired byproduct, since part of the formates are totally hydrogenated to CH₄ but part decompose yielding CO+H₂O.

Author contributions

Use this form to specify the contribution of each author of your manuscript. A distinction is made between five types of contributions: Conceived and designed the analysis; Collected the data; Contributed data or analysis tools; Performed the analysis; Wrote the paper.

For each author of your manuscript, please indicate the types of contributions the author has made. An author may have made more than one type of contribution. Optionally, for each contribution type, you may specify the contribution of an author in more detail by providing a one-sentence statement in which the contribution is summarized. In the case of an author who contributed to performing the analysis, the author's contribution for instance could be specified in more detail as 'Performed the computer simulations', 'Performed the statistical analysis', or 'Performed the text mining analysis'.

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Declaration of interests

- ☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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