Investigation on the Suitability of Engelhard Titanium Silicate as a Support for Ni-Catalysts in the Methanation Reaction

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Abstract: Methanation reaction of carbon dioxide is currently envisaged as a facile solution for the storage and transportation of low-grade energies, contributing at the same time to the mitigation of CO2 emissions. In this work, a nickel catalyst impregnated onto a new support, Engelhard Titanium Silicates (ETS), is proposed, and its catalytic performance was tested toward the CO2 methanation reaction. Two types of ETS material were investigated, ETS-4 and ETS-10, that differ from each other in the titanium content, with Si/Ti around 2 and 3% by weight, respectively. Catalysts, loaded with 5% of nickel, were tested in the CO2 methanation reaction in the temperature range of 300–500 °C and were characterized by XRD, SEM–EDX, N2 adsorption–desorption and H2-TPR. Results showed an interesting catalytic activity of the Ni/ETS catalysts. Particularly, the best catalytic performances are showed by Ni/ETS-10: 68% CO2 conversion and 98% CH4 selectivity at T = 400 °C. The comparison of catalytic performance of Ni/ETS-10 with those obtained by other Ni-zeolites catalysts confirms that Ni/ETS-10 catalyst is a promising one for the CO2 methanation reaction.

Keywords: methanation; carbon dioxide; nickel; titanium silicate

1. Introduction

The Power to Gas technology, based on the conversion of electricity to hydrogen via electrolysis, is regarded among the most environmentally sustainable approaches that could enable the chemical storage of energy [1]. However, hydrogen is not the appropriate medium for a storage application due to the significant compression (>100 bar) required to reach a moderate energy density. In contrast, the energy density of methane (CH4) is three times higher than hydrogen and facilities for transport and storage are widespread. Indeed, the methane can be produced converting hydrogen (H2) with carbon dioxide (CO2) following the well-known reaction (1) and easily stored as a renewable energy source:

$$4H_2(g) + CO_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \Delta H^\circ = -165 \text{ kJ mol}^{-1}$$ (1)

The carbon dioxide methanation reaction provides a solution for the storage and the transportation of low-grade energies. Moreover, it can potentially promote the abatement of polluting gas emissions since methane can be produced by simultaneously recycling carbon dioxide, CO2 [1–5]. Indeed, carbon oxides are regarded the major pollutants in the atmosphere, and their decrement represents a pressing challenge necessary to detect and limit their harmful effects [6,7].

Catalytic methanation reactors are typically operated at temperatures between 200 °C and 550 °C and at pressures ranging from 1 to 100 bar, since CO2 methanation is also a
strongly exothermic reaction and increasing the temperature is obviously unfavorable. However, it could be desirable to achieve higher conversions at the higher temperature when reagent gases (carbon monoxide, carbon dioxide and hydrogen) derive from other processes, such as the reforming of hydrocarbon coal gasification processes, or came from the exit-streams of the solid oxide electrolyzer cells (SOECs).

Despite several metals, such as Ni, Ru, Rh and Co, being used as catalysts [8], Ni is considered the best one due to its low cost and catalytic performance.

Alongside the active metal, the support of this phase plays a fundamental role. The support can improve the dispersion of active components and tunes the surface structure of the catalysts; these effects can influence the adsorption characteristics of the species involved and, consequently, the reaction pathways [2,9]. Among the support tested, SiO$_2$-based materials, such as zeolites, used as supports for metal catalysts, exhibit peculiar features such as ordered structures, high surface area, large pore volume and affinity versus CO$_2$ due to the intrinsic basicity of the support [10].

In the last years, different types of zeolites were used as metal supports to prepare active and stable catalysts [10]. Indeed, despite their massive utilization is mainly related to other specific applications, such as molecular sieves and adsorbent materials [11,12], their use in catalysis has manifold reasons: (i) the zeolite confinement effects (zeolite cages and channels intersections really act like nanoreactors, boosting catalysts’ activity); (ii) the possibility to adapt their basicity or acidity by both cationic exchange with alkaline metals and post-synthesis treatments (e.g., dealumination); and (iii) their hydrothermal stability that can be improved by steaming treatments.

Recently, Bacariza et al. have reviewed several works about the use of zeolite-based catalysts for carbon dioxide methanation, showing the potentiality of zeolites as support catalysts in this reaction. The type of zeolites more investigated are Y, A, X and ZSM-5, which essentially differ for framework structure and aluminum content [13].

The Engelhard Titanosilicate (ETS) is a microporous material that presents a structure similar to that of inorganic microporous zeolites [14], composed of tetrahedral SiO$_4$$^{4-}$ and octahedral TiO$_6$$^{8-}$ units [15]. ETS-4 (Na$_9$Si$_{12}$Ti$_5$O$_{38}$OH·12H$_2$O) and ETS-10 (M$_2$TiSi$_5$O$_{13}$H$_2$O with M = Na, K) both have a microporous structure but differ from each other in the Si/Ti ratio and in the pore size.

Few studies have employed the ETS material as catalyst support. In particular, in the dry reforming of methane, ETS-10 titanosilicate was proved to be an active and stable support for Ru species [16]. Philippou et al. [17] have used ETS-10 as Pt support in the hexane reforming, reporting that this material catalyzes the reaction with remarkably high selectivity. The mesoporous ETS-10 assembled Cu catalysts (named Cu/ETS-10-M) were also prepared and applied in the styrene functionalization reaction [18]. Santamaria and co-workers have investigated the use of Pt/ETS-10 catalyst for the selective oxidation of CO in the presence of H$_2$, CO$_2$ and H$_2$O concluding that the Pt–ETS-10 catalyst is active and selective in the above-mentioned reaction [19].

However, these materials, due to their porosity features, need more in-depth investigation to improve their application in the catalysis field.

In the present work, we investigated the suitability of ETS material as support for Ni catalyst in the methanation reaction. Ni/ETS-4 and Ni/ETS-10 catalysts have been prepared by impregnation method, characterized by different analytical techniques and tested in the methanation of carbon dioxide in the temperature range of 300–500 °C.

2. Results
2.1. Catalyst Characterization Results

X-ray diffraction patterns of synthesized ETS-4 (Figure 1, ETS-4 fresh) and ETS-10 (Figure 2, ETS-10 fresh) were found to be identical to the reference patterns reported in the literature (COD ID 4002324 and COD ID 7110493), confirming that the synthesized supports are pure ETS-4 and ETS-10.
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In order to check the support stability during the catalyst preparation, the XRD analysis was carried out after both the impregnation and reduction procedures (see Figures 1 and 2). Impregnation does not significantly modify the pattern of tested materials, but the reduction indeed destroyed the structure of ETS-4. In fact, in the related pattern (Figure 1, ETS-4 (r)), the only peak defined at around $2\theta = 44.6^\circ$ corresponds to the metallic nickel (COD ID 9013004) (enlargement in Figure 1). In addition, in the reduced Ni/ETS-10 (Figure 2, ETS-10 (r)) the peak related to the metallic nickel (enlargement in Figure 2) is detectable, and the broadness of this peak can be related to a very small particle size. The low thermal stability of ETS-4 is related to the hydrogen bonding between the extra framework water molecules and the framework oxygens, which leads to the formation of a vitreous amorphous phase [20].

Table 1 summarizes the main texture properties of supports and catalysts. The amount of deposited nickel is quite like the nominal content for both samples. The bare supports have microporous characteristics (the internal surface area is higher than the external one) and are characterized by a monomodal distribution in the range of micropores. The values of BET surface area of the as synthesized ETS are coherent to those reported in literature [21].

| Sample   | Si/Ti | Ni [w/w%] | $\text{SBET} [\text{m}^2/\text{g}]$ | $\text{Sext} [\text{m}^2/\text{g}]$ | $\text{Vmic} [\text{cm}^3/\text{g}]$ | $\text{Vmes} [\text{cm}^3/\text{g}]$ | Loss of Crystallinity [%] |
|----------|-------|-----------|----------------------------------|-----------------------------------|-----------------------------------|----------------------------|--------------------------|
| ETS-4 (f)| 1.90  | -         | 312                              | 279                               | 38                                | 0.12                       | 0.00                     |
| Ni/ETS-4 (i) | 1.87 | 4.86      | 270                              | 219                               | 56                                | 0.10                       | 0.00                     |
| Ni/ETS-4 (r) | 1.63 | 4.34      | 48                               | 4                                 | 46                                | 0.00                       | 0.18                     |
| ETS-10 (f)| 2.93  | -         | 386                              | 369                               | 47                                | 0.15                       | 0.00                     |
| Ni/ETS-10 (i) | 2.89 | 4.88      | 358                              | 313                               | 49                                | 0.14                       | 0.00                     |
| Ni/ETS-10 (r) | 2.90 | 4.97      | 312                              | 222                               | 96                                | 0.10                       | 0.05                     |

The micropore volumes of the two supports are close to the typical value of other microporous materials, (0.12 and 0.15 cm$^3$/g for ETS-4 and ETS-10, respectively). The contribution of the internal surface area to the total surface area, for both as-synthesized samples was very important (95% for ETS-10 and 90% for ETS-4). For both samples, the N$_2$ adsorption–desorption technique after the impregnation shows a reduction of the surface area value of ca. 13% for ETS-4 and of ca. 9% for ETS-10. However, all isotherms are of type IV, characteristic of microporous materials.

Figure 1. Diffraction pattern of fresh ETS-4 (f) and Ni/ETS-4 (i) after the impregnation treatment and Ni/ETS-4 (r) after the reduction treatment.

Figure 2. Diffraction pattern of fresh ETS-10 (f) and Ni/ETS-10 (i) after the impregnation treatment and Ni/ETS-10 (r) after the reduction treatment.

In order to check the support stability during the catalyst preparation, the XRD analysis was carried out after both the impregnation and reduction procedures (see Figures 1 and 2). Impregnation does not significantly modify the pattern of tested materials, but the reduction indeed destroyed the structure of ETS-4. In fact, in the related pattern (Figure 1, ETS-4 (r)), the only peak defined at around $2\theta = 44.6^\circ$ corresponds to the metallic nickel (COD ID 9013004) (enlargement in Figure 1). In addition, in the reduced Ni/ETS-10 (Figure 2, ETS-10 (r)) the peak related to the metallic nickel (enlargement in Figure 2) is detectable, and the broadness of this peak can be related to a very small particle size. The low thermal stability of ETS-4 is related to the hydrogen bonding between the extra framework water molecules and the framework oxygens, which leads to the formation of a vitreous amorphous phase [20].
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| Sample       | Si/Ti a | Ni a [w/w%] | SBET b m²/g | Sint c m²/g | Sext c m²/g | Vmic c cm³/g | Vmes d cm³/g | Loss of Crystallinity e [%] |
|--------------|---------|-------------|-------------|-------------|-------------|--------------|--------------|----------------------------|
| ETS-4 (f)    | 1.90    | -           | 312         | 279         | 38          | 0.12         | 0.00         | –                           |
| Ni/ETS-4 (i) | 1.87    | 4.86        | 270         | 219         | 56          | 0.10         | 0.00         | 46                          |
| Ni/ETS-4 (r) | 1.63    | 4.34        | 48          | 4           | 46          | 0.00         | 0.18         | 100                         |
| ETS-10 (f)   | 2.93    | -           | 386         | 369         | 47          | 0.15         | 0.00         | –                           |
| Ni/ETS-10 (i)| 2.89    | 4.88        | 358         | 313         | 49          | 0.14         | 0.00         | 8                           |
| Ni/ETS-10 (r)| 2.90    | 4.97        | 312         | 222         | 96          | 0.10         | 0.05         | 23                          |

a Determined by EDX analysis considering at least 20 points of investigation for three different magnifications; b Valued by BET model; c Valued by “t-plot” approach (Harkins-Jura reference equation); d Valued as difference of the Vmic by Vtot; e Valued as loss of intensity of the main peak respect the fresh sample.

The micropore volumes of the two supports are close to the typical value of other microporous materials, (0.12 and 0.15 cm³/g for ETS-4 and ETS-10, respectively). The contribution of the internal surface area to the total surface area, for both as-synthesized samples was very important (95% for ETS-10 and 90% for ETS-4). For both samples, the N₂ adsorption–desorption technique after the impregnation shows a reduction of the surface area value of ca. 13% for ETS-4 and of ca. 9% for ETS-10. However, all isotherms are of type I (results not shown for briefness); then for both structures, the Ni deposition by impregnation does not significantly affect nor the specific surface area of the final sample neither its microporous volume.

Reduction on Ni/ETS-10 causes a decrease in the internal surface area, i.e., micropore volume, compared with the parent material, whereas the external surface area increases. The N₂ adsorption isotherm of Ni/ETS-10 (not shown) after reduction exhibits a hysteresis loop at a relative pressure of 0.45–0.96, which is attributed to the presence of mesopores in the sample. In contrast, Ni/ETS-4 showed a more important loss of internal surface area with respect to the bare ETS-4. This causes an important decrease of the micropore volume of Ni/ETS-4, which is almost zero compared to the parent material. This behavior can be explained by incipient structure collapse, as confirmed by XRD (Figure 1); the collapse of the structure is responsible of the complete loss of the microporous area.

Despite the collapse of crystalline structure, the morphology of ETS-4 is not fully destroyed after the treatments of impregnation and reduction, as shown in Figure 3. The bare sample exhibits a morphology identified as “cuboids”, namely an intergrown polycrystalline form wherein small plate crystals grow in tandem to form more complex aggregate shapes [22]. The largest crystal measured approximately 2 µm × 20 µm × 5 µm (a × b × c) for cuboids. The dimensions for the largest individual plates (which make up the cuboids), were less than one-tenth of their intergrown cuboid dimensions. The treatment of impregnation does not modify the morphology of the support, but the reduction treatment promotes a “dissolution” of crystal in agreement with the XRD observations.
The samples based on ETS-10 support exhibit a cubic shape intergrown morphology with multimodal distribution. The crystal habit is not altered like the ETS-4 based samples by impregnation and reduction step (Figure 4). The distribution of nickel on the ETS-10 surface was regular as mapped by EDX (Figure 4), and metal crystal size was estimated equal to 9.2 nm (±0.6 nm) through the Debye–Scherrer relation, as elsewhere reported [3].

To study the reducibility of nickel precursor species and the metal–support interaction, TPR-H$_2$ experiments were performed.

The TPR profiles showed different sets of H$_2$ consumption peaks, as displayed in Figure 5. However, for both samples, the peaks at lower temperature (367 °C for ETS-4 and 336 °C for ETS-10) can be attributed to the reduction of Ni species located outside of the structure and, therefore, are more easily reducible. In contrast, the peaks located at higher temperature (415 °C for ETS-4 and 392 °C for ETS-10) can be correlated to the nickel species located within the zeolite super cages [23]. These peaks for ETS-4 were shifted to higher temperature with respect to ETS-10: this means a greater interaction of Ni species with the ETS-4 support. At higher temperature, in the TPR profile of ETS-4 a shoulder and broader peak at 500 °C appears, due to the changing of the titanium reduction state from +4 to +3 state [24].

Comparing the TPR-H$_2$ behavior of nickel-based support of ETS with the other zeolite supports, such as zeolite Y and zeolite Beta [25], it is possible to observe that ETS has a better reducibility of Ni-species, which depends on the low nickel/ETS interactions.

2.2. Catalytic Tests Results

Carbon dioxide methanation was performed over bare ETS supports and Ni/ETS catalysts in the temperature range 300–500 °C. As expected, due to the absence of the active catalytic phase, ETS-4 and ETS-10 supports did not exhibit any catalytic activity, whereas results of Ni based catalysts are reported in the Figure 6. On a dry basis, the only products observed in the outlet gas stream are methane and carbon monoxide.
Carbon dioxide methanation was performed over bare ETS supports and Ni/ETS catalysts in the temperature range 300–500 °C. As expected, due to the absence of the active RWGS (reverse water gas shift) reaction [26]. Further increase in the reaction temperature at 500 °C led to a slightly decrease in the CO₂ conversion (55% for Ni/ETS-4 and 60% for Ni/ETS-10) due to thermodynamic limit of methanation reaction and to the occurrence of the reverse water gas shift reaction [26].

Both catalysts Ni/ETS-4 and Ni/ETS-10 reached optimum conversion at 400 °C, and when the temperature was increased up to 500 °C, the CO₂ and H₂ conversions were reduced due to the thermodynamic limitations of CO₂ methanation. Indeed, the Ni/ETS-4 showed ca. 11% CO₂ conversion at 300 °C, which increased to ca. 62% at 400 °C, and Ni/ETS-10 showed ca. 29% of CO₂ conversion at 300 °C, which increased to ca. 67% at 400 °C, remaining below the thermodynamic limits; this could be due to the greater kinetic barrier for the full reduction of CO₂ (+4) to CH₄ (−4), an eight-electron process that obviously requires high activation energy [26]. Further increase in the reaction temperature at 500 °C led to a slightly decrease in the CO₂ conversion (55% for Ni/ETS-4 and 60% for Ni/ETS-10) due to thermodynamic limit of methanation reaction and to the occurrence of RWGS (reverse water gas shift) reaction [26].
Figure 6. CO₂ and H₂ conversion of samples Ni/ETS-4 (a) and Ni/ETS-10 (b) in the temperature range 300–500 °C.

The CH₄ selectivity results are showed in Figure 7. For Ni/ETS-4, the CH₄ selectivity increases from ca. 29% at 300 °C to 42% at 400 °C and then decreases to ca. 2% at 500 °C. In contrast, the CH₄ selectivity increases for Ni/ETS-10 from ca. 56% at 300 °C and to 98% at 400 °C and then decreases to 35.4% at 500 °C (Figure 7). Apparently, this phenomenon was not thermodynamically consistent, because methane concentration should decrease by increasing the temperature, due to the methanation equilibrium; this suggests that the methanation on the Ni/ETS catalysts at relative low temperatures (Tₘ > 400 °C) was probably a kinetics-controlled reaction [27].

Despite the profiles of CH₄ selectivity for both catalysts are similar, the values of CH₄ selectivity in the range of temperature examined are very different (Figure 7).

Ni/ETS-10 allows obtaining a selectivity value at 400 °C close to 100%; in contrast, at the same temperature, the selectivity of CH₄ reached by Ni/ETS-4 catalyst is lower than the half.

The different behavior of the ETS-4 and ETS-10 can be related to the content of titanium in the framework of the zeolitic structure. The ETS-4 has a higher titanium content that determines the low thermal stability of the impregnated sample, as verified by XRD.
diffraction results of the reduced samples (Figure 1). Although the zeolite structure is not preserved, the dispersion of the active metal catalysts is still observed, as indeed confirmed by EDX analysis (Figure 3) and by the high values of conversion. Then, in order to elucidate how the catalytic performance of nickel supported on titanium silicate is affected, the methanation reaction, in the same operative conditions and at the temperature of 400°C, has been carried out using silicon dioxide (S718483 Sigma–Aldrich, \( S_{\text{BET}} 175 \text{ m}^2/\text{g} \)) and titanium dioxide (637262 Sigma–Aldrich Titanium (IV) oxide, \( S_{\text{BET}} 50 \text{ m}^2/\text{g} \)) as nickel supports, loading the supports with the same amount of metal. In Figure 8, the comparison of conversion and selectivity values for all supports tested at \( T = 400 \text{ °C} \) are reported. Both supports exhibit a higher value of \( \text{CO}_2 \) conversion with respect to titanium silicate, but the \( \text{CH}_4 \) selectivity for Ni catalysts supported on titanium dioxide is consistently lower than all other catalysts. Then, the catalyst based on titanium silicate ETS-4 performs worse value of \( \text{CH}_4 \) selectivity because it is loaded with higher content of titanium. Moreover, during the reduction procedure, with the collapse of zeolites structure, there is a leaching of titanium from the framework, and at the same time, the titania undergoes a reduction to \( \text{TiO}_x \) (\( x < 2 \)). This titanium species covers the nickel particles that, although they remain in their metallic state, are encapsulated by Ti suboxides (\( \text{TiO}_x \)) after thermal treatment, in agreement with Pan et al. [28]. \( \text{TiO}_x \) species addresses the \( \text{CO}_2 \) dissociation, decreases the hydrogen dissociation and then probably causes the change in the selectivity of products [29].

![Figure 8. Comparison of different supports for Ni catalysts in the methanation reaction at \( T = 400 \text{ °C} \) and GHSV 30,000 h\(^{-1}\).](image)

Catalysts supported on ETS-10, after reaction, retain the zeolitic structure and the featuring morphology, as showed in the Figure 9. Comparing these results with those obtained by other researcher that used zeolites materials as Ni support for \( \text{CO}_2 \) methanation in similar reaction conditions, the ETS-10 appears to be a promising support for Ni catalyst in the methanation reaction (Table 2).
An interesting comparison can be carried out between Ni catalyst supported on ETS-10 and zeolite Beta is that these supports, in fact, have topological similarities. Both these materials have three-dimensional pore systems, almost identical, although the zeolite Beta is an aluminosilicate composed of tetrahedral SiO$_4^{4-}$ and AlO$_4^{5-}$ units, whereas ETS-10 is a titanosilicate composed of tetrahedral SiO$_4^{4-}$ and octahedral TiO$_6^{8-}$ units [15,30–32]. Comparing the catalytic activity of Ni/ETS-10 and Ni/Beta (Table 2), it was observed that, despite the lower loading and the higher GHSV employed for Ni/ETS-10, it still exhibits better catalytic activity as compared to Ni/Beta catalyst.

Table 2. Summary of CO$_2$ methanation performance of Ni/zeolites catalysts at high temperature reaction (T > 350 °C).

| Catalyst Composition | H$_2$/CO$_2$ | GHSV [h$^{-1}$] | T [°C] | CO$_2$ Conversion | CH$_4$ Selectivity | Ref. |
|----------------------|-------------|-----------------|-------|-------------------|-------------------|------|
| 5% NiY               | 4:1         | 43,000          | 450   | 50                | 95                | [23] |
| 5% NiSilicalite      | 4:1         | 60,000          | 450   | 57                | 91                | [24] |
| 5% Ni/ETS-10         | 4:1         | 30,000          | 400   | 68                | 98                | [This work] |
| 5% Ni/ETS-10         | 4:1         | 30,000          | 350   | 52                | 90                | [This work] |
| 10% NiHY             | 4:1         | 10,000          | 350   | 15                | 88                | [33] |
| 10% NiNaY            | 4:1         | 10,000          | 350   | 30                | 82                | [33] |
| 10% Ni/HBeta         | 4:1         | 10,000          | 350   | 23                | 82                | [33] |
| 10% Ni/NaBeta        | 4:1         | 10,000          | 350   | 33                | 88                | [33] |
| 15% Ni/HBeta         | 4:1         | 16,000          | 350   | 80                | 79                | [33] |
| 15% Ni/HBeta         | 4:1         | 16,000          | 400   | 76                | 75                | [25] |

For this material, each TiO$_6$ unit contributes two minus charges to the framework, leading to the framework oxygen atoms in TiO$_6$ unit bearing negative charges, regarded as the basic sites [34,35]. For CO$_2$ adsorption, providing the basic sites on the catalyst surface likely improve CO$_2$ uptake via acid–base interaction. Further, the CO$_2$ uptake increases in the presence of oxygen vacancies on the support, ascribed as an adsorption site for CO$_2$ molecules [36]. Oxygen vacancies can be formed within reducible support (TiO$_2$, CeO$_2$, ZrO$_2$, etc.) since the oxygen vacancy can be mobile inside the lattice and plays an important role in the redox process. The presence of defected sites on Ni/ETS-10 was probably due to the incipient support mesoporosity, indirectly confirmed by the loss of crystallinity introduced after the reduction treatment.

The differences in the catalytic performance between the different Ni-based zeolite supports (Table 2) can be then ascribed to the different zeolite framework, both from a compositional and topological point of view, that influences: (i) the interaction and affinity...
with CO$_2$ and (ii) the metal support interactions, affected by the spatial arrangement and bond angles present in the microporous materials.

3. Experimental Section

3.1. Catalyst Preparation

The two different types of Engelhard Titanium Silicates, namely ETS-4 and ETS-10, were synthesized according to a procedure reported elsewhere [33,37].

Ni catalysts were prepared by the incipient wetness impregnation method. The metal precursor (nickel nitrate hexahydrate Ni(NO$_3$)$_2$·6H$_2$O (Sigma–Aldrich, Saint Louis, MO, USA) was opportune solubilized in an ethanol solution and dispersed over the ETS support, with a total metal content of 5 wt%. After the impregnation process, catalysts were dried at 120 °C for 24 h; subsequently, a mixture of 10 vol% H$_2$ in He flow was used to reduce catalysts at 500 °C for 2 h, using the same heating and cooling rates. Samples were characterized both after the impregnation/dry process and after the reduction treatment.

3.2. Catalysts Characterization

The identification of phases in fresh, impregnated/dry, reduced and spent catalysts was performed by powder X-ray diffraction (XRD) using a Bruker D2 Phaser using CuK$_\alpha$ radiation at 30 kV and 20 mA (Bruker, Karlsruhe, Germany). Peaks attribution was made according with COD (Crystallographic Open Database). The diffraction angles 2θ were varied between 10° and 80° in steps of 0.02° and a count time of 5 s per step.

The reduction of metal oxides was monitored by the temperature programmed reduction (TPR), carried out with a Chemisorb Micromeritics 2750 instrument (Micrometrics, Norcross, GA, USA) under a flux of 50 cm$^3$ min$^{-1}$ of 10 vol.% H$_2$/Ar in the temperature range 25–1000 °C at atmospheric pressure.

A Phenom Pro-X scanning electron microscope equipped with an energy-dispersive X-ray (EDX) spectrometer was utilized for SEM analysis (Deben, Suffolk, UK). The EDX analysis was used to evaluate the content and dispersion of metal, acquiring for all samples at least 20 points of investigation at three different magnifications. The counting time for the EDX analysis was 120 s. The results were found to be reproducible to less than ±5% for all samples.

The porous features of the samples were determined by equilibrium adsorption and desorption isotherms of N$_2$ at 77 K with a Micromeritics ASAP 2020 instrument. Before the analysis, all samples were pre-treated in vacuum condition at 200 °C for 12 h. In order to determine the total surface area of the samples, the data collected were modeled using the BET equation, which is more suitable for solids containing micropores. The evaluation of microporous volumes, internal and external surface area and V–t curves were also interpreted by the “t-plot” method using the Harkins–Jura reference isotherm [38].

3.3. Catalytic Test

CO$_2$ methanation was carried out in a quartz tubular fixed-bed reactor (1 cm inner diameter, 25 cm length) horizontally placed in a furnace under atmospheric pressure. A mixture gas of H$_2$/CO$_2$/N$_2$ with fixed molar ratio 4/1/1 was fed into the reactor by mass flow controllers (Brooks Instrument, Smart Mass Flow). An Agilent 6890 Plus gas chromatograph equipped with thermal conductivity (TCD) and flame ionization (FID) detectors was used to on-line analyze reactants and products every 20 min. N$_2$ was used as internal standard for mass balance calibration.

Activity tests (8 h each) were carried at fixed temperature in the range $T = 300–500$ °C and space velocity $\text{GHSV} = 30,000$ h$^{-1}$. The total flow rate was 50 cc/min, and GHSV was defined as follows: $\text{GHSV} = \text{Volumetric flow velocity of gas}/\text{Volume of catalyst}$.

The CO$_2$ and H$_2$ conversion were calculated, on dry basis, by the following formula: $X_{\text{CO}_2} = (\text{moles CO}_2 \text{ IN} – \text{moles CO}_2 \text{ OUT})/\text{moles CO}_2 \text{ IN}$; $X_{\text{H}_2} = (\text{moles H}_2 \text{ IN} – \text{moles H}_2 \text{ OUT})/\text{moles H}_2 \text{ IN}$. 
The selectivity of methane was defined as follows: 

\[ S_{\text{CH}_4} = \frac{\text{moles CH}_4 \text{ produced}}{\text{moles of total products}}. \]

All reactions were repeated three times, and the deviation measured for the results was ±4%. The conversion and selectivity were calculated referring to the stationary values registered when the profile of conversion/selectivity versus time was stable and the phenomenon of deactivation had not occurred yet.

4. Conclusions

The performance of Ni supported on ETS-4 and ETS-10 was investigated. The novel supports were characterized and tested toward the methanation reaction in the range \( T = 300–500 \, ^\circ \text{C} \).

The results showed a potential catalytic activity of the Ni/ETS-10 catalyst, characterized by 68% \( \text{CO}_2 \) conversion and 98% \( \text{CH}_4 \) selectivity at \( T = 400 \, ^\circ \text{C} \).

The ETS-4 was demonstrated to be not a suitable support for the Ni catalyst because of the collapse of the structure, due to the thermal treatment carried out to obtain the catalyst. In addition, the leaching of titanium species had a detrimental effect on the selectivity toward methane.

Ni/ETS-10 retained its framework zeolitic structures and in comparison to other microporous materials exhibited superior catalytic performance.

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