Carbon Dioxide Reforming of Methane over Nickel-Supported Zeolites: A Screening Study

Carmen Bacariza 1,*; Leila Karam 2,3,*; Nissrine El Hassan 3,4; José M. Lopes 1 and Carlos Henriques 1

1 Centro de Química Estrutural (CQE), Departamento de Engenharia Química, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049 001 Lisboa, Portugal; jmlopes@tecnico.ulisboa.pt (J.M.L.); carlos.henriques@tecnico.ulisboa.pt (C.H.)
2 Laboratoire de Réactivité de Surface, Campus Pierre et Marie Curie, Sorbonne Université, UMR CNRS 7197, 4 Place Jussieu, 75005 Paris, France
3 Department of Chemical Engineering, Faculty of Engineering, University of Balamand, Amioun P.O. Box 33, El Koura, Lebanon; nissrine.elhassan@lau.edu.lb
4 Petroleum Engineering Program, School of Engineering, Lebanese American University, Byblos P.O. Box 36, Lebanon
* Correspondence: maria.rey@tecnico.ulisboa.pt (C.B.); karam@kofo.mpg.de (L.K.)

Abstract: As the utilization of zeolites has become more frequent in the dry reforming of methane (DRM) reaction, more systematic studies are required to evaluate properly the influence of zeolites’ composition and framework type on the performance. Therefore, in this work, a step-by-step study was performed with the aim of analyzing the effects of Ni loading (5, 10 or 15 wt.% over USY(3) zeolite), Si/Al ratio (3, 15 or 38 on USY zeolites with 15 wt.% Ni) and framework type (USY, BEA, ZSM-5 or MOR for 15 wt.% Ni and Si/Al ratios of ≈40) on catalysts’ properties and performances.

Increasing Ni loadings enhanced CH₄ and CO₂ conversions even though the catalysts’ stability was decreasing over the time. The variation of the Si/Al ratio on USY and the use of different zeolites had also a remarkable impact on the catalytic performance. For instance, at 500–600 °C reaction temperatures, the catalysts with higher basicity and reducibility exhibited the best results. However, when the temperature was further increased, catalysts presenting stronger metal–support interactions (nickel nanoparticles located in mesoporous cavities) displayed the highest conversions and stability over time. In brief, the use of 15 wt.% Ni and a USY zeolite, with both micro- and mesopores and high surface area, led to the best performances, mainly attributed to a favorable number of Ni⁰ active sites and the establishment of stronger metal–support interactions (due to nanoparticles confinement inside the mesopores).

Keywords: dry reforming of methane; syngas production; nickel; zeolites; structure–reactivity

1. Introduction

Currently, an important effort is required for increasing the share of renewables in the global energy system in order to accomplish the international climate goals [1]. That being said, a potential alternative could be the use of wastes such as sewage sludge, agricultural and crop residues, animal dung, industrial organic wastes, or wastewaters for the production of biogas through anaerobic digestion [1]. Biogas, composed mainly of CH₄ and CO₂, can be then used for the production of biomethane (through upgrading and purification [2]) or even syngas (CO and H₂; through reforming strategies). Consequently, biogas constitutes an attractive renewable carbon source, and its exploitation is advantageous from both financial and environmental points of view.

Among the different alternatives for syngas production, steam reforming is the one already implemented on an industrial scale and leads to H₂/CO ratios of ≈3. However, the simultaneous utilization of carbon dioxide and methane for the production of syngas (dry reforming of methane, DRM: CO₂ + CH₄ → 2CO + 2H₂) represents a promising...
alternative, especially for the production of syngas with low H₂/CO ratio (≤1), potentially applied in the synthesis of oxygenated compounds such as methanol, acetic acid, or other long chain hydrocarbons [3]. Despite its interest, DRM is still an immature industrial process due to the highly endothermic nature of the reaction, requiring high operating and investment costs, in addition to catalysts deactivation due to sintering and carbonaceous species formation [2,4].

Typically, dry reforming catalysts contain noble (e.g., Ru, Rh, Pd, Pt) or transition (e.g., Ni, Co) metals supported over CeO₂, La₂O₃, ZrO₂, MgO, SiO₂, Al₂O₃, MOFs, or even zeolites [3–7]. Noble metals present resistance to deactivation, but their high cost and low availability limit their industrial application [2]. In this way, the cost-effectivity of Ni-based catalysts motivates further developments in the enhancement of their properties in order to design highly active, selective and stable materials [2]. According to literature [5], the main properties to guarantee in DRM catalysts should be: (i) strong metal-support interaction; (ii) high metal dispersion; (iii) basicity; (iv) oxygen storage capacity; (v) favored reducibility; and (vi) high porosity and surface areas. Therefore, the use of micro- and mesoporous supports allows for having high surface areas and porosities, leading to promising results as seen previously for mesoporous materials such as MSN, KCC-1, SBA-15, SBA-16 or MCM-41 [2,8–11]. Furthermore, nickel-based zeolites (e.g., ZSM-5, BEA, MOR, Y, FER, Silicalite-1, ITQ-6) have been applied in this reaction [12–29] due to their typical thermal stability, shape selectivity, and easily tunable properties [3].

Among the different studies using Ni-containing zeolites as supports for DRM catalysts, Alotaibi et al. prepared several La and Ca-promoted 10 wt.% Ni catalysts by wet impregnation method and using two Y zeolites with different Si/Al ratios (2.5 and 6) as supports [24]. Samples were tested at 700 °C under atmospheric pressure using a CH₄:CO₂ ratio of 1:1 and Ni/Y and Ca-Ni/Y catalysts presented the highest CH₄ conversion, but the stability decreased over time. On the contrary, La-Ni/Y was more stable but had lower performances both in terms of CH₄ and CO₂ conversion. This catalytic behavior was attributed to the nature of the metal–support interactions in the presence of different promoters and supports [24]. Furthermore, Fakeeha et al. prepared 5 wt.% Ni catalysts over γ-Al₂O₃ and two zeolite supports (H-USY and H-ZSM-5), and evaluated the effect of the calcination temperature (500, 700, and 900 °C) on the results [14]. Samples were tested at 500, 600, and 700 °C under atmospheric pressure using a CH₄:CO₂ ratio of 1:1 and higher stability with lower carbon deposition found for Ni/H-ZSM-5 (catalysts’ stability varied as follows: Ni/H-ZSM-5 > Ni/γ-Al₂O₃ > Ni/H-Y) [14]. Inoue et al. [23] prepared Ni-supported H-MOR (Si/Al = 10), Na-MOR (Si/Al = 10), and H-Y (Si/Al = 2.6) zeolites as well as Al₂O₃ catalysts and tried also to mix the most promising materials to boost the activity. Authors verified that Ni-H-MOR and Ni-Al₂O₃ catalysts led to the highest activity and stability. When comparing to other zeolites, a complete destruction of H-Y zeolite was observed during the tests, which justified its remarkable lower activity. However, authors did not consider that using two zeolites with different Si/Al ratios, responsible for modifications in several properties, could limit the interpretation of the results. Dai et al. prepared Ni-Pt catalysts using Silicalite-1 (S-1) as support [26]. Authors reported the encapsulation of Ni and Pt nanoparticles inside the zeolite channels, which led to sintering and coking resistance and emphasized on the fact that the bimetallic catalyst performed better than the monometallic ones. That being said, Pinheiro et al. dealuminated Na-Y (Si/Al = 5.6) and Na-BEA (Si/Al = 13) commercial zeolites for using them as supports for bimetallic Ni-Pt catalysts [20]. Authors declared that dealumination by steaming led to the formation of mesopores in both types of zeolites, with Ni and Pt particles highly dispersed in these cavities, increasing the acidity and improving the accessibility of the reactants to the active sites. However, they found that Ni/Zeolites were inactive for DRM due to high coke deposition, and Ni-Pt/Zeolites showed better performances than Pt/Zeolites. This effect was attributed to the enhancement of carbon dioxide adsorption close to Ni⁰ sites, reacting with carbon deposits. Needless to say, BEA samples presented better results (activity and stability) due to the improved accessibility, while Y samples exhibited lower
activity due to their acidity, hindering the elimination of carbon deposits [20]. Finally, Frontera et al. [29] compared ≈5 wt.% Ni-supported Silicalite-1, MCM-41 and delaminated zeolite ITQ-6 catalysts performances toward DRM. Even if Ni-ITQ-6 presented the best results, Ni-Silicalite-1 exhibited the highest H$_2$/CO ratio and the lowest carbon deposition. Authors concluded that increasing the number of defects (e.g., silanol groups) on the supports’ surface promotes the formation of smaller and well-dispersed metal particles, boosting performances.

As mentioned earlier, tuning the Al content on zeolites’ framework (and hence, the Si/Al ratio) and changing the type of structure used led to important changes in the physicochemical properties and performances toward DRM. However, the evaluation of these effects requires a systematic study under the same experimental conditions. Consequently, in the present work, a systematic series of Ni/Zeolites with different Ni loadings (5, 10 and 15 wt.%), Si/Al ratios (3, 15 and 38), and zeolite framework type (USY, BEA, MOR, ZSM-5) were analyzed to assess the influence of these parameters on the physicochemical properties and performances toward DRM reaction. Samples were prepared by ion-exchange of commercial zeolites followed by in cipient wetness impregnation with nickel and characterized by chemical analysis, N$_2$ sorption, CO$_2$ sorption, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), diffuse reflectance spectroscopy UV-Vis (DRS UV-Vis), H$_2$ temperature programmed reduction (H$_2$-TPR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Finally, samples were catalytically tested in dry reforming of methane reaction.

2. Materials and Methods

2.1. Catalysts Preparation

USY, BEA, ZSM-5, and MOR commercial zeolites, without a significant number of extra-framework aluminium (EFAL) species, Si/Al ratios ranging from 3 to 47 and provided by Grace Davison and Zeolyst, were used as starting materials for the preparation of a series of Ni-containing Na-Zeolites (Table 1).

| Code       | Preparation Method | Na Loading $^1$ (wt.%) | Si/Al$_{\text{global}}$ $^1$ | Ni $^1$ (wt.%) |
|------------|-------------------|-----------------------|-----------------------------|----------------|
| USY(3)     | IE $^2$           | 2.7                   | 3                           | -              |
| 5Ni/USY(3) | IWI $^3$          | 2.7                   | 3                           | 5              |
| 10Ni/USY(3)| IWI $^3$          | 2.7                   | 3                           | 10             |
| 15Ni/USY(3)| IWI $^3$          | 2.7                   | 3                           | 15             |
| USY(15)    | IE $^2$           | 0.8                   | 15                          | -              |
| 15Ni/USY(15)| IWI $^3$       | 0.8                   | 15                          | 15             |
| USY(38)    | IE $^2$           | 0.3                   | 38                          | -              |
| 15Ni/USY(38)| IWI $^3$        | 0.3                   | 38                          | 15             |
| BEA(38)    | IE $^2$           | 0.3                   | 38                          | -              |
| 15Ni/BEA(38)| IWI $^3$       | 0.3                   | 38                          | 15             |
| ZSM-5(40)  | IE $^2$           | 0.7                   | 40                          | -              |
| 15Ni/ZSM-5(40)| IWI $^3$      | 0.7                   | 40                          | 15             |
| MOR(47)    | IE $^2$           | 0.7                   | 47                          | -              |
| 15Ni/MOR(47)| IWI $^3$        | 0.7                   | 47                          | 15             |

$^1$ Determined by ICP analysis; $^2$ IE: ion exchange; $^3$ IWI: incipient wetness impregnation.

In order to reduce the potential impact of the compensating cation nature in the performances and physicochemical properties, all zeolites (initially containing Na loadings ranging from <0.1 to 2.1 wt.% according to ICP analysis) were ion-exchanged with a NaNO$_3$ solution using a volume/mass ratio of 4 mL $g_{\text{zeolite}}^{-1}$, room temperature and 4 h of stirring [30,31]. Samples were filtered using distilled water, dried overnight at 100 °C and,
after repeating the process three times, calcined at 500 °C under air flow for 6 h and using a heating rate of 2 °C min⁻¹. Finally, the incorporation of Ni (5, 10, and 15 wt.% for USY(3) and 15 wt.% for the rest of supports) over the final Na-Zeolite supports was accomplished by incipient wetness impregnation, using nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma Aldrich, >99%) as metal precursor. After drying overnight at 80 °C, catalysts were calcined at 500 °C for 6 h under air flow, being finally named as xNi/y/(z) with x referring to the Ni loading (confirmed by ICP analysis in all cases), y to the zeolite framework type (USY, BEA, ZSM-5, or MOR), and z to the Si/Al global ratio (also determined by ICP analysis).

2.2. Characterization Techniques

Catalysts elemental analysis was performed by inductively coupled plasma (ICP) to determine the composition of the prepared samples in terms of Ni, Si, Al, and Na loadings. N₂ and CO₂ sorption measurements were carried out at −196 °C and 0 °C, respectively, on an Autosorb iQ equipment from Quantachrome. Before adsorption, samples were degassed under vacuum at 90 °C for 1 h and then at 350 °C for 4 h. The total pore volume (V_total) was calculated from the adsorbed volume of N₂ at a relative pressure (p/p₀) of 0.95, whereas the micropores volumes (V_microp) and external surface areas (S_ext) were determined using the t-plot method. Mesopores (and/or intercrystalline spaces) volumes (V_meso) were given by the difference V_total − V_microp. Powder XRD patterns were obtained in a Bruker AXS Advance D8 diffractometer, using Cu Kα radiation and operating at 40 kV and 40 mA. The scanning range was set from 5 to 80° (2θ), with a step size of 0.03°/2 s. Thermogravimetric analyses (TGA-DSC) were performed on a Setsys Evolution TGA from Setaram instruments. Samples (35–40 mg) were first saturated in water and then heated between 20 and 400 °C (10 °C min⁻¹) under air flow (30 mL min⁻¹). Then, the interaction of water with the samples in terms of strength was characterized as done in our former studies [31] by determining an index (I) reported by Anderson et al. [32], calculated as the ratio between the mass loss at 150 and 400 °C. TGA was also used to characterize spent catalysts, by performing analysis from room temperature to 800 °C (10 °C min⁻¹). In addition, DRS spectra in the UV-Vis region were obtained in a Varian Cary 5000 UV-Vis-NIR spectrophotometer equipped with a diffuse reflectance accessory in the 200–800 nm range. Reflectance spectra were converted into the Schuster–Kubelka–Munk (SKM) function (F(R)) and presented versus wavelength to evaluate the presence of the different nickel species in the samples. Additionally, NiO band gaps were calculated by plotting F(R)² as a function of the energy (E = hc/λ) and extrapolating the linear region to F(R)² = 0 [33–35]. The final band gap energies can depend on the combination of two factors: the average size of the metal particles and the strength of the interaction between the metal and the support [36–40]. An increase of the band gap energy is usually observed with the decrease of the size of the Ni particles [36,37]. H₂-TPR experiments were performed in a Micromeritics AutoChem II equipment, where catalysts were first pretreated at 250 °C under argon flow and then cooled down to the room temperature. After that, the reduction of the catalysts was carried out under a 5%H₂/Ar flow, increasing the temperature from room temperature to 900 °C (10 °C min⁻¹) and monitoring the hydrogen consumption using a TCD detector. SEM analysis was performed for parent zeolites using a Hitachi S2400 microscope. Finally, TEM analysis was performed for the pre-reduced samples using a HREM 2010 JEOL LaB₆ microscope (200 kV). Average Ni⁰ particle sizes were determined by using ImageJ® software (>100 particles counted for each catalyst).

2.3. Catalytic Tests

Catalysts were tested in a Hastelloy-X tubular reactor with an internal diameter of 9 mm, using a Microactivity reference catalytic reactor (EFFI, PID Eng, and Tech Spain). Catalysts (powder form, particle size < 63 μm) were loaded into the reactor mixed with quartz (inert) and reduced in situ at 470 °C for 2 h in a 5%H₂/Ar flow (30 mL min⁻¹). The catalytic bed length/catalyst particle diameter ratio was >150, while the reactor diameter/catalyst particle diameter ratio was >143. After pretreatment, dry reforming of methane
was conducted under atmospheric pressure using a CH$_4$/CO$_2$ ratio of 1:1 and a total GHSV of 72 L g$^{-1}$ h$^{-1}$ (0.050 g of catalyst per test). Good reproducibility of catalytic results under these conditions was obtained. For activity measurements, the reaction temperature was increased from 470 °C (5 °C min$^{-1}$) up to 650 °C and kept at 650 °C for 12 h. The gaseous products were then analysed online by a micro-GC equipped with a TCD detector and two columns (Plot U and Molecular sieves) in parallel. CH$_4$ and CO$_2$ conversions as well as the H$_2$/CO ratios were calculated using the molar flows (F) of the reactants and products, as shown in Equations (1)–(3):

\[
\text{CH}_4 \text{ conversion } \% = \frac{F_{\text{CH}_4(\text{in})} - F_{\text{CH}_4(\text{out})}}{F_{\text{CH}_4(\text{in})}} \times 100
\]

\[
\text{CO}_2 \text{ conversion } \% = \frac{F_{\text{CO}_2(\text{in})} - F_{\text{CO}_2(\text{out})}}{F_{\text{CO}_2(\text{in})}} \times 100
\]

\[
\frac{\text{H}_2}{\text{CO}} = \frac{F_{\text{H}_2}}{F_{\text{CO}}}
\]

3. Results

3.1. Structural and Textural Properties

Catalysts’ XRD patterns are illustrated in Figure 1. As seen, most of the catalysts exhibited diffraction peaks ascribed to NiO phases at ≈37, ≈43, and ≈63° [41], being NiO crystallite sizes of 18–26 nm determined by Scherrer equation for all 15 wt.% Ni-containing samples. These peaks were not clear in the case of 5Ni/USY(3) and 10Ni/USY(3), probably due to the lower metal content. Additionally, it can be verified that the impregnation of Ni over the studied zeolite supports did not lead to structural changes in the zeolites, as the characteristic diffraction peaks of USY, BEA, ZSM-5, and MOR zeolites were still observed at 5–40° [42] in the metal-loaded samples’ patterns.

Regarding the textural properties assessed by N$_2$ sorption (Table 2; isotherms in Figure S1), it could be seen that USY(3) was mainly a microporous zeolite with a considerably low mesoporous volume ($V_{\text{meso}} = 0.04 \text{ cm}^3 \text{ g}^{-1}$). The incorporation of different Ni loadings over this support led to a reduction in both microporous volumes ($V_{\text{micro}}$) and external surface areas ($S_{\text{ext}}$). While the first effect could be related to the lower accessibility of N$_2$ to the zeolite pores due to the location of NiO particles in the pore entries blocking the access, the second could suggest a deposition of the NiO species on the external surface of the zeolite. It is clear that samples with higher Si/Al ratios, USY(15) and USY(38), presented significantly higher $V_{\text{meso}}$ and $S_{\text{ext}}$ values, which could be ascribed to the postsynthesis dealumination treatments carried out for the preparation of these commercial zeolites [43]. Indeed, Leveque et al. [43] reported that USY(15) and USY(38) zeolites (commercially named as CBV 720 and CBV 780, respectively), were obtained from a lower Si/Al ratio zeolite (named as CBV 300) by a combination of leaching and steam dealumination treatments. This was reported to result in the formation of disrupted crystal morphologies, cracks and voids (mesoporosity) [43]. Indeed, the mesoporous cavities/holes present in these samples could be observed in complementary TEM micrographs of 15Ni/USY(15) and 15Ni/USY(38) presented in Figure S2. Again, Ni impregnation decreased the $V_{\text{micro}}$, $V_{\text{meso}}$, and $S_{\text{ext}}$ values in these samples, which could be attributed to the location of NiO species on the external surface and/or inside the created mesopores [31]. Regarding the framework type, BEA(38) zeolite presented more relevant $V_{\text{meso}}$ and $S_{\text{ext}}$ values due to the intercrystalline spaces present in this zeolite [44]. The considerably smaller crystallite size of BEA(38) zeolite when comparing to USY(38), ZSM-5(40), or MOR(47) can be confirmed by the SEM micrographs presented in Figure S3. The aggregates of such small crystallites are known to generate intercrystalline spaces that could act as mesoporous cavities able to locate metal particles [44]. The reduction of the $V_{\text{meso}}$ in this sample after Ni incorporation suggested the location of NiO species inside these intercrystalline spaces acting as mesopores, as it could be seen in Figure S2. In addition, the slight variation in terms of $V_{\text{micro}}$
after nickel incorporation over BEA(28) zeolite (from 0.15 to 0.11 cm$^3$ g$^{-1}$) suggested that the slight reduction in BEA diffraction peaks’ intensity after Ni addition (Figure 1) could not be ascribed to a structural damage. Finally, in ZSM-5(40) and MOR(47), the impact of Ni incorporation in the textural properties was similar to that observed in USY(3), as these were essentially microporous zeolites.

3.2. Reducibility

Catalysts’ reducibility is depicted in the H$_2$-TPR profiles presented in Figure 2. To be pointed out is that, according to previous XRD data, nickel was present as NiO in all catalysts. Consequently, its reduction is expected to occur through the following reaction: $\text{NiO} + \text{H}_2 \rightarrow \text{Ni}^0 + \text{H}_2\text{O}$. As seen, the higher the metal loading the most relevant the fraction of NiO species located on the external surface of the USY(3) zeolite (reduction processes at 300 to 400 $^\circ$C, as reported in literature [41,45]), in accordance with the previously discussed impact of Ni addition in the textural properties. It can be observed that the higher the USY zeolites’ Si/Al ratio the greater the fraction of NiO species located inside the mesopores of the zeolites (reduction processes at 500 to 650 $^\circ$C [31]), as previously noticed through the analysis of the textural properties evolution and in agreement with literature [46–49]. Finally, in terms of framework type, a more important fraction of NiO reduced above 500 $^\circ$C could be observed for 15Ni/BEA(38) zeolite when comparing with the corresponding ZSM-5 and MOR samples. This confirmed the presence of NiO particles in the intercrystalline spaces of this zeolite acting as mesopores [46–48]. Furthermore, in the case of ZSM-5 and MOR samples, NiO species were mainly located on their external surface,
probably due to the absence of large cavities for the accommodation of NiO particles in these structures. Indeed, the presence of a small reduction peak at higher temperatures in these last zeolites could be attributed to a heterogeneous distribution of the NiO particles in terms of size [50–52]. In short, H2-TPR data clearly showed that Ni loading and zeolites’ composition and structure type are clearly responsible for modifications in the metal–support interactions, manifested in the different reducibility behaviors.

Table 2. Textural properties obtained using N2 sorption for all the samples from the present work and the corresponding supports.

| Catalyst     | Vmicro (cm³ g⁻¹) | Vmeso (cm³ g⁻¹) | Sext (m² g⁻¹) |
|--------------|------------------|-----------------|---------------|
| USY(3)       | 0.30             | 0.04            | 17            |
| 5Ni/USY(3)   | 0.28             | 0.03            | 13            |
| 10Ni/USY(3)  | 0.21             | 0.03            | 14            |
| 15Ni/USY(3)  | 0.22             | 0.03            | 14            |
| USY(15)      | 0.25             | 0.27            | 250           |
| 15Ni/USY(15) | 0.19             | 0.19            | 159           |
| USY(38)      | 0.20             | 0.29            | 325           |
| 15Ni/USY(38) | 0.19             | 0.19            | 165           |
| BEA(38)      | 0.15             | 0.59            | 203           |
| 15Ni/BEA(38) | 0.11             | 0.36            | 51            |
| ZSM-5(40)    | 0.11             | 0.10            | 140           |
| 15Ni/ZSM-5(40)| 0.09            | 0.07            | 99            |
| MOR(47)      | 0.17             | 0.11            | 77            |
| 15Ni/MOR(47) | 0.14             | 0.08            | 57            |

Figure 2. H2-TPR profiles of: (A) Ni loading samples: (a) 5Ni/USY(3), (a’) 10Ni/USY(3), and (a’’) 15Ni/USY(3); (B) Si/Al ratio samples: (b) 15Ni/USY(3), (b’) 15Ni/USY(15), and (b’’) 15Ni/USY(38); (C) Framework type samples: (c) 15Ni/USY(38), (c’) 15Ni/BEA(38), (c’’) 15Ni/ZSM-5(40), and (c’’)’ 15Ni/MOR(47).

3.3. Surface Properties

Catalysts were also characterized in terms of their affinity with water due to the possible inhibitory effect of H2O in DRM, related with the occurrence of RWGS (CO₂ + H₂ → CO + H₂O) as a side reaction [4]. As done in previous works [31,53], TGA-DSC experiments were carried
out for determining the h indexes, indicators of catalysts’ hydrophobicity. Higher Ni loadings slightly increased the interaction strength with water, while higher Si/Al ratios led to more hydrophobic materials (Table 3). However, no clear tendency could be found in terms of zeolite framework type, with relatively similar h indexes obtained for BEA(38), ZSM-5(40) and MOR(47) samples when comparing with 15Ni/USY(38).

Table 3. h indexes (from TGA-DSC), NiO band gaps (BG; from DRS UV-Vis), Ni\(^0\) average sizes and dispersions (from TEM) obtained for all the samples from the present work.

| Catalyst            | Calcinised | Reduced at 470 °C |
|---------------------|------------|-------------------|
|                     | h Index    | BG\(_{NiO}\) (eV) | Ni\(^0\) size (nm) | Standard Deviation (nm) | Dispersion (%) |
| 5Ni/USY(3)          | 0.52       | 3.7              | 19                | 7                     | 5              |
| 10Ni/USY(3)         | 0.60       | 3.7              | 18                | 7                     | 5              |
| 15Ni/USY(3)         | 0.61       | 3.7              | 18                | 7                     | 5              |
| 15Ni/USY(15)        | 0.86       | 3.8              | 28                | 11                    | 3              |
| 15Ni/USY(38)        | 0.91       | 3.8              | 25                | 9                     | 3              |
| 15Ni/BEA(38)        | 0.78       | 3.7              | 18                | 6                     | 5              |
| 15Ni/ZSM-5(40)      | 0.76       | 3.7              | 24                | 10                    | 4              |
| 15Ni/MOR(47)        | 0.84       | 3.7              | 23                | 12                    | 4              |

DRS UV-Vis spectra were also collected (Figure 3). As observed, all samples presented the characteristic bands of NiO at \(\approx 300\), \(\approx 380\), \(\approx 410\), and \(\approx 720\) nm [41,45]. In addition, NiO band gap energies were determined (Table 3), with comparable obtained values for all samples.

Finally, the affinity of the samples toward CO\(_2\) was characterized by the collection of CO\(_2\) isotherms (Figure 4), as done in literature [54–58]. While similar results were obtained for 5 and 15 wt.% Ni containing USY(3) zeolite samples, suggesting that CO\(_2\) affinity is not strongly influenced by the Ni loading, samples with different Si/Al ratios presented significantly different behaviors. Indeed, zeolites basicity is related to the Si/Al ratio since...
CO$_2$ interacts with zeolites’ compensating cations forming carbonate-like species [30,59], thus depending on its nature and content [30]. The nature of the cations is the same in all samples from this work (Na$^+$), but the content depends on the number of framework Al species leading to negative charges. Thus, zeolites with higher Si/Al ratios (lower number of framework Al atoms) are expected to be less basic [56,60,61]. This effect was confirmed in the obtained isotherms, where CO$_2$ uptakes decreased for all the relative pressures when increasing the Si/Al ratio (Table 1). In terms of the framework type effect, CO$_2$ uptakes for a chosen relative pressure followed the order: 15Ni/MOR(47) > 15Ni/ZSM-5(40) > 15Ni/BEA(38) >> 15Ni/USY(38). These results could be again attributed to the amount of Na$^+$ in the samples (ion exchange degrees of 38, 43, 86, and 94% for USY(38), BEA(38), ZSM-5(40) and MOR(47) samples, respectively, with H$^+$ occupying the remaining cationic positions). Furthermore, the type of structure could induce different interactions with sodium cations, which could modify the nature of the interactions with CO$_2$ molecules. Indeed, even if the Si/Al ratios chosen were similar in these four samples, the cations exchange capacity is strongly influenced by the framework type, probably due to accessibility issues.

Figure 4. CO$_2$ isotherms collected at 0 °C for: (A) Ni loading and Si/Al samples: (a) 5Ni/USY(3), (a’) 15Ni/USY(3), (a’’) 15Ni/USY(15), and (a’’’) 15Ni/USY(38); and (B) Framework type samples: (b) 15Ni/USY(38), (b’) 15Ni/BEA(38), (b’’) 15Ni/ZSM5(40), and (b’’’) 15Ni/MOR(47). Note that the y-axis is different in both graphs, to clearly see differences between the isotherms obtained for samples presented in (B).

3.4. Metal Particles Size

TEM micrographs were collected for all samples after reduction under H$_2$ flow at 470 °C (Figure 5; histograms presented in Figure S4). By analyzing the micrographs, the average Ni$^0$ particle sizes and metallic dispersions were obtained (Table 3). For USY(3) support and Ni contents from 5 to 15 wt.%, the estimated average Ni$^0$ sizes were 18–19 nm and metallic dispersions 5%, being concluded that the studied metal loadings did not strongly influence these parameters. Regarding the samples with increasing Si/Al ratios, no clear correlation was observed, contrary to what was reported in literature for Ni/BEA samples with Ni contents lower than 4 wt.% where the increase of the Si/Al ratio favored the metallic dispersion [38]. Moreover, one can note that, for higher Si/Al ratios, the standard deviation was slightly higher and the dispersion lower (3%), indicating a more heterogeneous distribution of the Ni$^0$ particles in these samples. This could be due to the presence of nickel particles both on the external surface and inside the mesopores of
the zeolites (see Figure S2). Finally, regarding the framework type effect, 15Ni/USY(38), 15Ni/ZSM-5(40) and 15Ni/MOR(47) samples showed similar average Ni\(^0\) particle sizes while 15Ni/BEA(38) presented the smallest Ni\(^0\) particles and the highest dispersion (5%).

![TEM micrographs collected for the samples from the present work after reduction with H\(_2\) at 470 °C.](image)

**Figure 5.** TEM micrographs collected for the samples from the present work after reduction with H\(_2\) at 470 °C.

### 3.5. Catalytic Performances towards DRM

#### 3.5.1. Nickel Loading Effect

In terms of catalytic performances towards DRM, Figure 6 illustrates CH\(_4\) (Figure 6A) and CO\(_2\) (Figure 6B) conversions for all Ni/USY(3) zeolites with increasing Ni loadings as a function of the reaction temperature. As verified, higher temperatures led to higher conversions in all cases because of the endothermic nature of this reaction. Higher Ni loadings clearly promoted the catalytic performances, which means that the additional amount of Ni (leading to higher metallic surface areas as the average Ni\(^0\) particle sizes were 18–19 nm in all samples) boosted the number of active sites enhancing the results, in accordance with literature [62–64]. Stability tests were also done at 650 °C and the catalytic results are shown in Figure 6C as a function of time-on-stream. Complementary results are also found in Figure S5 (CH\(_4\) and CO\(_2\) conversions at 0, 200, 450, and 700 min) and Table S1 (conversion losses, %, after 200, 450 and 700 min). As observed, 15Ni/USY(3) still possessed higher CO\(_2\) and CH\(_4\) conversions than 5Ni/USY(3) and 10Ni/USY(3) catalysts after 13 h. All catalysts demonstrated CO\(_2\) conversions higher than CH\(_4\) conversions, which is due to the simultaneous occurrence of RWGS, consuming CO\(_2\). This behavior was more obvious in the case of 15Ni/USY(3), which exhibited a H\(_2\):CO ratio below 1 (≈0.85), stressing on the production of more CO than H\(_2\). In addition, samples with 10 and 15 wt.% Ni showed a decrease of 15–16% in the conversions during the long-term tests (Table S1), while 5Ni/USY(3) presented higher stability (7–8% decrease). This behavior could be related to the weaker metal–support interactions present in catalysts with higher Ni loadings, being the occurrence of sintering processes and even coke deposition favored.
Figure 6. Variation of (A) CH₄ and (B) CO₂ conversion levels as a function of temperature (500–650 °C) and (C) CH₄ conversion, CO₂ conversion and H₂:CO molar ratio as a function of time on stream (T= 650 °C) during DRM (P = 1 atm, CH₄:CO₂ = 1:1, GHSV = 72 L g⁻¹ h⁻¹) over 5Ni/USY(3), 10Ni/USY(3) and 15Ni/USY(3) catalysts. Thermodynamic values of CH₄, CO₂, and H₂:CO (straight black line) in (C) were calculated using the HSC 7.1 software.

Catalysts were analyzed by XRD (Figure S6) and TGA (Figure S7) after tests. The three spent samples exhibited diffraction peaks ascribed to Ni⁰ phases at 44.5, 51.9 and 76° (Figure S6). In addition, the presence of graphitic carbon (2θ = 27 and 54.4°) was clear in 10 and 15 wt.% Ni-containing samples. Furthermore, a structural damage of the zeolite could be suggested for 15Ni/USY(3), as faujasite zeolite diffraction peaks could not be clearly identified in 2θ = 5–40° range, given that this phenomenon was already reported in literature by Inoue et al. [23]. In terms of TGA profiles (Figure S7), two main mass loss processes were observed below 400 °C, attributed to water desorption [65], and above 450 °C, ascribed to coke volatilization/decomposition [65,66] and/or zeolites dehydroxylation [65,67,68]. Thus, by comparing the profiles above 450 °C in the three USY(3)-based catalysts, it could be concluded that the use of higher Ni loadings led to formation of more coke, in accordance with the literature [62].

3.5.2. Si/Al Ratio Effect

Complementary, when using a constant Ni loading (15 wt.%), the same zeolite structure (USY) and increasing Si/Al ratios (3, 15 or 38), 15Ni/USY(3) exhibited the best conversions at 500–600 °C (Figure 7A,B). This could be related to the fact that 15Ni/USY(3) presented higher basicity than the 15Ni/USY(15) and 15Ni/USY(38) catalysts, as proved also in the CO₂ adsorption curves seen in Figure 4. In fact, mechanistic considerations...
regarding DRM reaction have pointed out that the increase in basicity is an important factor to limit carbon deposition [69,70]. However, the best performances and higher stability over the time were exhibited by catalysts with higher Si/Al ratios at 650 °C. This behavior could be related to the stronger interaction between nickel nanoparticles and USY support in these samples. For instance, the presence of mesopores in zeolites with higher Si/Al ratios led, as seen by the previous analysis of the H$_2$-TPR profiles, to the location of NiO nanoparticles in these cavities (confinement effect), inducing stronger metal–support interactions and preventing sintering and even coke deposition, as seen in Ni-based mesoporous silica catalysts in literature [69]. Complementary, and due to the occurrence of RWGS reaction (CO$_2$ + H$_2$ → CO + H$_2$O), the interaction of the samples with water could present an eventually remarkable effect in the performances. Indeed, when RWGS is a side-reaction, favored by higher reaction temperatures [71], the formation of water is expected during the reaction, leading to deactivation and sintering, besides the potential negative effect in the zeolite structure (steaming). Consequently, a weaker interaction between these molecules and the zeolite-based catalysts could avoid H$_2$O to be adsorbed over the zeolite sites responsible for CO$_2$ activation (e.g., compensating cations [72]), at the same time that eventual deactivation processes due to water could be hindered. The hydrophobic character of higher Si/Al ratio zeolites (Table 2) could thus reduce the inhibitory effect of water in the reaction.

Figure 7. Variation of (A) CH$_4$ and (B) CO$_2$ conversion levels as a function of temperature (500–650 °C) and (C) CH$_4$ conversion, CO$_2$ conversion and H$_2$:CO molar ratio as a function of time on stream (T= 650 °C) during DRM (P = 1 atm, CH$_4$:CO$_2$ = 1:1, GHSV = 72 L g$^{-1}$ h$^{-1}$) over 15Ni/USY(3), 15Ni/USY(15) and 15Ni/USY(38) catalysts. Thermodynamic values of CH$_4$, CO$_2$, and H$_2$:CO (straight black line) in (C) were calculated using the HSC 7.1 software.
Catalysts were also analyzed using XRD and TGA after reaction tests (Figure S6 and Figure S7, respectively). Results indicated that higher Si/Al ratio zeolites exhibited a lower resistance towards coke deposition (diffraction peaks ascribed to carbon in XRD patterns and important mass loss above 450 °C in TGA profiles), in agreement with the previously discussed impact of the basicity in carbon formation prevention. Furthermore, the clearer identification of faujasite peaks in the 5–40° range in spent 15Ni/USY(15) and 15Ni/USY(38) patterns could indicate that the weaker interaction between water and these zeolites hindered the occurrence of steaming processes able to damage or partially destruct USY structure. On the contrary, the higher hydrophilicity of 15Ni/USY(3) could be responsible for the occurrence of more relevant steaming processes, damaging the structure, as suggested by the less intense zeolite diffraction peaks in this sample after test.

3.5.3. Framework Type Effect

In the last study, and considering the higher activity and stability exhibited by 15Ni/USY(38) at 650 °C, the effect of the zeolite framework type in the performances was assessed over BEA, ZSM-5, and MOR zeolites with Si/Al ratios of ≈40 and impregnated with 15 wt.% Ni, with the results presented in Figure 8.

![Figure 8](image-url)

Figure 8. Variation of (A) CH₄ and (B) CO₂ conversion levels as a function of temperature (500–650 °C) and (C) CH₄ conversion, CO₂ conversion, and H₂:CO molar ratio as a function of time on stream (T = 650 °C) during DRM (P = 1 atm, CH₄:CO₂ = 1:1, GHSV = 72 L g⁻¹ h⁻¹) over 15Ni/USY(38), 15Ni/BEA(38), 15Ni/ZSM-5(40), and 15Ni/MOR(47) catalysts. Thermodynamic values of CH₄, CO₂, and H₂:CO (straight black line) in (C) were calculated using the HSC 7.1 software.
As previously observed for Si/Al ratio series, two tendencies were verified in terms of CO$_2$ and CH$_4$ conversions at different temperatures (Figure 8A,B). Indeed, while at 500–600 °C, the order was the following: 15Ni/MOR(47) > 15Ni/ZSM-5(40) > 15Ni/USY(38) ≈ 15Ni/BEA(38); at higher temperatures, similar conversions were exhibited by 15Ni/USY(38) and 15Ni/MOR(47), with 15Ni/BEA(38) being the less performing catalyst. As previously analyzed by the collection of CO$_2$ adsorption isotherms, the order of basicity (related to a greater exchange degree of Na$^+$ in the structure) was the following: 15Ni/MOR(47) > 15Ni/ZSM-5(40) > 15Ni/BEA(38) >> 15Ni/USY(38). This trend is indeed equivalent to the ones found for the activities below 600 °C, agreeing with previous considerations on the effect of basicity in the Si/Al ratio zeolites series. In terms of stability over time at 650 °C (Figure 8C), USY(38) and MOR(47)-based catalysts presented the best results (relative and absolute conversion losses of 12–23% and 8–15%, respectively; Table S1), followed by 15Ni/ZSM-5(40) and 15Ni/BEA(38), with the last two significantly reducing their activity after 12 h (relative and absolute conversion losses of 36–55% and 18–32%, respectively; Table S1). As previously pointed out, the favored metal–support interactions found in 15Ni/USY(38) and its higher hydrophobicity could be the reason of the improved performances (activity and stability) exhibited at higher temperatures by this sample.

Spent catalysts were again characterized by XRD (Figure S6) and TGA (Figure S7). As seen both in XRD patterns and TGA profiles, carbon deposits were present in all catalysts, especially on MOR(40) and ZSM-5(40)-supported ones. These two catalysts presented the highest basicity which, as previously seen, should hinder coke decomposition. However, based on literature [62], larger Ni$^0$ crystallites enhance the formation of carbon deposits and these two samples presented less dispersed nickel nanoparticles, mostly located on their outer surface.

### 3.6. Comparison with Literature

Finally, the most stable and active catalysts from this work, 15Ni/USY(38) and 15Ni/MOR(47), were compared to other Ni-supported catalytic systems from literature (Table 4). As verified, conversion losses below 15% were verified for both catalysts from this work after 12 h under reaction conditions. These results were similar or better than other found in literature for Ni-based catalysts. However, the significant differences in terms of operating conditions limit the establishment of direct comparisons.

| Catalyst               | Ni (wt.%) | Temperature (°C) | GHSV (L·g$^{-1}$·h$^{-1}$) | Time (h) | Initial X (%) | Final X (%) | H$_2$:CO | Ref. |
|------------------------|-----------|------------------|-----------------------------|----------|---------------|-------------|---------|------|
| Ni/ZrO$_2$             | 13        | 700              | 38                          | n.a.     | 70            | 80          | 13      | 20   | 0.31 | [73] |
| Ni/La$_2$O$_3$         | 5         | 700              | 300                         | 15       | 90            | 92          | 70      | 80   | 1.03 | [74] |
| Ni/Al$_2$O$_3$         | 10        | 700              | n.a.                        | 108      | 68            | 92          | 68      | 90   | 0.6  | [75] |
| Ni/γ-Al$_2$O$_3$       | 10        | 750              | 50                          | 10       | 61            | 63          | 32      | 29   | 0.88 | [76] |
| Ni/γ-Al$_2$O$_3$       | 15        | 700              | 12                          | 8        | 65            | 82          | n.a.    | n.a. | 0.92 | [77] |
| Ni/θ-Al$_2$O$_3$       | 3         | 800              | 60                          | 20       | 98            | 62          | n.a.    | n.a. | 0.78 | [78] |
| Ni/Al$_2$O$_3$         | 10        | 650              | 16                          | 4        | 40            | n.a.        | 0       | n.a. | 0.79 | [79] |
| Ni/Zeolite A           | 7         | 700              | 30                          | 5        | 70            | 85          | 13      | 20   | 0.31 | [64] |
| Ni/Zeolite X           | 7         | 700              | 36                          | 14       | 90            | 92          | 58      | 70   | 1.03 | [80] |
| Ni/ZSM-5               | n.a.      | 600              | 14                          | 100      | 29            | 42          | 20      | 33   | n.a. | [81] |
| Ni/MCM-41              | 10        | 760              | 20                          | 72       | 82            | 90          | 65      | 80   | 0.9  | [82] |
| Ni/MCM-41              | 2         | 750              | 50                          | 72       | 94            | n.a.        | 50      | n.a. | 0.9  | [83] |
| Ni/SBA-15              | 10        | 600              | 20                          | 30       | 52            | 87          | 39      | 70   | 0.8  | [84] |
| Ni/ZrO$_2$             | 15        | 750              | 24                          | 10       | 90            | 98          | 69      | 70   | n.a. | [85] |
| Ni/MgAl$_2$O$_4$       | 10        | 750              | 50                          | 10       | 84            | 92          | 84      | 92   | 0.98 | [76] |
| Ni/USY                 | 15        | 650              | 72                          | 12       | 66            | 67          | 51      | 54   | 1.0  | This work |
| Ni/MOR                 | 15        | 69               | 61                          | 58       | 69            | 69          | 61      | 58   | 1.1  | |

Table 4. Comparison of the most outstanding catalysts from this work with others from literature.
4. Discussion

Based on the previous results and in order to establish structure–reactivity correlations, the relative variation of the main catalysts’ properties reported for DRM reaction [5] in the three studies from this work was analyzed and shown in Figure 9.

Figure 9. Comparison of catalysts’ properties for: (A) Ni loading; (B) Si/Al ratio; and (C) Framework type samples.

Starting by the Ni loading series (Figure 9A), as previously observed in Figure 6, the activity was enhanced by the increase of metal content while a higher stability was shown by 5Ni/USY(3). The increase in the CO$_2$ and CH$_4$ conversions could be clearly ascribed to the increment in the number of nickel active sites when increasing Ni loading,
as reducibility at lower temperatures was enhanced while no significant modifications in the dispersion/average Ni\(^0\) size were verified. In addition to this, the higher stability of 5Ni/USY(3) over the time could be ascribed to the stronger metal–support interactions in this sample. Indeed, the incorporation of a lower metal loading induced a more homogeneous distribution of the nanoparticles both on the external surface and inside zeolite’ cavities, improving the interaction with the zeolite sites and avoiding agglomeration processes responsible for catalyst deactivation.

Regarding the USY zeolites with variable Si/Al ratios (Figure 9B), it could be concluded that the modification of this parameter affected catalysts’ properties in opposite directions. Indeed, while the metallic dispersion was not strongly affected, the textural properties and metal–support interactions were favored by the decrease of the Al content. Indeed, the dealumination processes carried out commercially to produce these zeolites were responsible for the formation of cavities acting as mesopores, increasing the mesoporous volumes and the external surface areas, and allowing the encapsulation of nickel nanoparticles inside the structure. On the contrary, the basicity, dependent on the number of aluminum atoms in the zeolite, as well as NiO species’ reducibility at lower temperatures, were favored by lower Si/Al ratio zeolites. When analyzing the catalytic performances (Figure 7), the improved basicity and reducibility of lower Si/Al ratio zeolites could explain the higher performances below 600 °C. On the contrary, the higher textural properties and its consequent effect on the metal–support interactions through nanoparticles confinement inside mesopores could explain the higher conversions attained by higher Si/Al ratio zeolites above 600 °C. In addition, another property not reported in literature as relevant for this reaction, the hydrophobicity (improved for higher Si/Al ratios), could play a prominent role at higher temperatures in the prevention of zeolites’ structure collapse due to steaming processes as well as in the reaction mechanism, as water (produced via RWGS reaction) is adsorbed on the same sites as CO\(_2\) in the case of zeolites, leading to an inhibitory effect.

Finally, regarding the framework type (Figure 9C), 15Ni/MOR(47) and 15Ni/ZSM-5(40) exhibited the best basicity (due to the higher Na\(^+\) loading) and reducibility (due to the purely microporous structure inducing a major location of NiO species on zeolites’ external surface). In addition, the highest textural properties and strongest metal–support interactions were found in 15Ni/USY(38), while 15Ni/BEA(38) presented only the best features in terms of metallic dispersion. For instance, catalytic performances (Figure 8), were more promising below 600 °C for 15Ni/MOR(47) and even 15Ni/ZSM-5(40) catalysts, which, as seen in the study of the Si/Al ratio effect, could be ascribed to the better basicity and reducibility of NiO species in these materials. On the contrary, at higher reaction temperatures, the conversions and stability over the time were improved for 15Ni/USY(38), probably due to the nanoparticles encapsulation inside its mesopores (stronger metal–support interactions) and, eventually, the weaker interaction with water molecules.

5. Conclusions

In this work, the influence of the Ni loading, the Si/Al ratio, and the framework type on the properties and performances of Ni-based zeolites towards DRM reaction was analyzed. For this purpose, three catalysts series were systematically prepared, characterized, and finally tested. In terms of Ni loading effect, studied over 5, 10 and 15 wt.% Ni catalysts supported over a USY zeolite with a Si/Al ratio of 3 (USY(3)), the increase of this parameter was found to improve both CO\(_2\) and CH\(_4\) conversions at different reaction temperatures. This effect was ascribed to the increase in the number of nickel active sites, as no significant differences in terms of metallic dispersion were found among the samples. Using 15 wt.% Ni, the effect of the Si/Al ratio was studied over three USY supports (USY(3), USY(15) and USY(38)). Based on the results, using lower Si/Al ratio zeolites was beneficial for the activities below 600 °C, while the tendency was the opposite at higher temperatures. Similarly, when analyzing the influence of the framework type by comparing USY(38) to BEA(38), ZSM-5(40), and MOR(47) as supports, the last two zeolites showed the best
activities below 600 °C, while using USY(38) was found as more favorable at higher reaction temperatures. Thus, it was observed that the more basic catalysts with easily reducible NiO species exhibited higher performances below 600 °C, while, at harsher conditions, the existence of stronger metal–support interactions due to nanoparticles confinement in mesoporous cavities and even the weaker interaction with water (product of RWGS reaction able to adsorb in the same sites as CO₂) were identified as key for understanding the better performances.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10071331/s1, Figure S1: N₂ isotherms; Figure S2: Additional TEM micrographs; Figure S3: SEM micrographs of parent zeolites; Figure S4: Histograms of reduced catalysts; Figure S5: CH₄ and CO₂ conversions at 0, 200, 450, and 700 min of on-stream during long-term tests; Figure S6: Diffractograms of the Ni containing spent samples; Figure S7: TGA profiles of spent samples; Table S1: Relative and absolute CH₄ and CO₂ conversion losses during long-term tests.

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