Renewable Energy Storage in the Natural Gas Network: Enhancing CO_2 Conversion into Synthetic Natural Gas over Zeolite Catalysts by Tuning Ni Particle Size

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ABSTRACT. Power-to-gas constitutes a promising strategy for renewable electricity surplus storage in the natural gas network during low demand periods. In this way, developing suitable CO_2 methanation catalysts is mandatory for the application of this process under scale-up conditions. Zeolites have been reported as interesting supports for Sabatier reaction catalysts due to their tune-able properties in terms of affinity with CO_2 and H_2O. Even if in the literature mostly Ni-based zeolites have been studied, Ni^0 particles supported on monometallic zeolite catalysts typically present average sizes in the range of 20-25 nm, being required high metal loadings (10-15 wt.%) for obtaining competitive CH_4 yields.

To overcome this issue and in the context of Clean 4G project (POCI-01-0247-FEDER-038323), in this work three strategies have been followed with the final purpose of improving Ni-based catalysts dispersion over an optimized zeolite support (Cs-USY). Firstly, the incorporation of promoters such as Ce, Zr, La and Y together with Ni (co-impregnation) was studied. In a second step, the effect of the impregnation solvent used in the preparation of monometallic Ni/Cs-USY catalysts was verified, by comparing water, ethanol, methanol, 2-propanol, acetone and ethylene glycol. Finally, the application of a new synthesis method of nickel nanoparticles, sol-gel, was explored. All catalysts were applied in CO_2 methanation reaction and characterized using TGA, XRD and H_2-TPR. Yttrium was found as the most favourable promoter, 2-propanol as the best solvent and sol-gel technique did not favour the performances due to the larger Ni particle sizes formed (50 nm).

Keywords: CO_2 methanation, zeolite-supported catalysts, promoters, impregnation solvent, sol-gel method.

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1. Introduction

Climate change is one of the most important worldwide environmental issues nowadays. In addition, renewable energy sources have been extensively used to help in climate issues but their intermittency can compromise grid stability. So, there is need for possible surplus renewable energy storage solution to help with the intermittency of this renewable energy. In this way, power-to-gas has been reported as a promising alternative since, by this strategy, the surplus electricity can be used to produce renewable hydrogen (H_2) which can further react with CO_2 to give synthetic natural gas (CH_4).

The activation of the carbon dioxide requires the use of catalysts. Indeed, several noble metals (Rh, Ru, Pd) and VIIIB group elements (especially Ni) based on different supports such as Al_2O_3, SiO_2, Ce/Zr mixed oxides, mesoporous materials, carbon, hydrotalcite-derived materials or even zeolites have been studied and reported in the literature. Among all, Ni-based zeolites gained attention in recent times due to their tunable properties [1][2][3][4]. Indeed, monometallic Ni samples based on zeolite supports presented good performances, irrespective of their relatively large particle sizes (20-25 nm) and the main location of the metal particles on the outer surface, probably due to the enhanced metal-support interactions established [4]. However, the main drawback of these systems remains in the sintering of Ni species leading to Ni^0 particles in the range of 20-25 nm. Consequently, further efforts must be done for improving metallic dispersion in Ni based catalyst. To avoid deactivation, several strategies related with the preparation or even composition of materials is reported in literature.

One of the strategies to improve metallic phase dispersion in supported Ni based catalysts is to incorporate promoters. Several promoters have been studied in literature (e.g. transition metals, noble metals, lanthanides, group alkali earth metals). Indeed, Trovarelli *et al.* [5] prepared Rh/SiO_2 catalysts promoted with CeO_2 and compared them with un-promoted Rh/SiO_2 and Rh/CeO_2 samples. Authors verified that the activity of the original catalysts was greatly enhanced by the addition of CeO_2 as promoter. Authors attributed this beneficial effect of Ce addition to the surface vacancies created at the interface between Rh and reduced CeO_2, enhancing CO_2 activation. Additionally, similar positive effects of CeO_2 addition were reported by Rahmani *et al.* [6] for Ni based catalysts supported on mesoporous material γ-Al_2O_3. Also, Boix *et al.* [7] prepared Pt-Co mordenite with different loadings of both metals verifying that bimetallic samples presented better performances in terms of activity in comparison monometallic catalysts, with the best Co/Pt ratio being 0.6. The promoting effect of Pt was attributed to the increase in hydrogen activation and the formation of intermediate active species $PtCo_xO_y$.

Furthermore, according to the literature, the nature of the impregnation solvent can also positively affect the metal-support interactions. Qiu *et al.* [8] prepared Ni nanoparticles over SBA-15 by co-impregnation using ethylene glycol (EG) for reforming reaction of methane and they found out that EG addition improved resistance to sintering and proved to be thermal stable in dry reforming of methane. Zhang *et al.* [9] prepared Co catalysts supported on silica for Fischer Tropsch synthesis (FTS) reaction using different solvents to check the effects on the properties of the silica support, metal dispersion and species reducibility. The use of ethanol led to the smallest cobalt particles and the highest metallic dispersion. Ho and Su [10] studied the effect of ethanol as impregnation solvent for Co supported on SiO_2. They found that ethanol presented a positive effect due to the increased interaction between Co and SiO_2, which resulted in the decrease in crystal size of cobalt species.

Finally, other strategy which could eventually lead to smaller Ni particles is to tune the preparation method. Branco *et al.* [11] studied Ni-based bimetallic catalysts prepared by sol-gel method for partial oxidation of methane. They found that the synthesized materials were active and selective for the studied application as methane conversion was 50-70 % and syngas selectivity to H_2 and CO were 60-90 % and 50–80 %, respectively, even at relatively low reaction temperatures (550-650 ^{0}C). Also, Danial *et al.* [12] performed experiments with NiO nanoparticles prepared by sol-gel in electro-catalytic oxidation of glucose. They verified that the performances were significantly enhanced by this preparation method, even at less favorable reaction conditions.

Hence, present work deals with the study of influential effects of promoters' incorporation, impregnation solvent, and even change of preparation method (Pechini-modified sol-gel method) with special focus in obtaining well dispersed metallic phase in Ni/zeolites based catalysts for CO_2 methanation.

2. Experimental

2.1. Catalysts preparation

As a first step, an optimized zeolite support was prepared by taking into account previous studies carried out in this research group [1][2][3][4]. Consequently, a commercial USY zeolite supplied by Zeolyst containing a global Si/Al ratio of 38 was modified in order to obtain the Cs-USY form chosen as support for this work. The preparation was carried out by using a certain mass of commercial USY zeolite (12 g) and mixing it with a 1 M $CsNO_3$ solution keeping a $V_{solution}/m_{zeolite}$ = 4 ml g^{-1}. The suspension was continuously stirred for 4 h at room temperature and then filtered under vacuum with distillated water until neutral pH = 7 was achieved. Finally the sample was dried in oven overnight at 100 ^{0}C. This procedure was repeated three times and then calcination was carried out at 500 ^{0}C under air flow (60 ml min^{-1} g^{-1}) for 6 h using a heating rate of 2 ^{0}C/min.

In first approach, the **effect of adding different promoters** (M = Ce, Zr, La, Y) over Ni-based Cs-USY catalysts was evaluated. Samples were prepared by co-impregnating 15 wt.% Ni and 15 wt.% promoter over the support [13]. Indeed, Ni and promoters precursor salts were used for preparing an aqueous impregnation solution incorporated to the support in a drop wise manner under continuous stirring. Samples were then dried overnight at 80 ^{0}C and calcined at 500 ^{0}C for 6 h.

In second approach, the effect of the **impregnation solvent** nature (water, ethanol, methanol, 2-propanol, acetone or ethylene glycol) in the characteristics and performances of Ni/Cs-USY catalysts containing 15 wt. % of Ni incorporated by incipient wetness impregnation was studied. For incipient wetness impregnation, a solution of $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich, >99%) prepared by using a solvent volume close to the zeolite pores was added drop wise to the Cs-USY support under continuous stirring. After this, drying in oven at 80 ^{0}C and calcination were carried out.

In last study, one of the methods commonly applied for preparing nanoparticles **(sol-gel)** was explored. In this way, NiO nanoparticles were prepared by Pechini modified method [14][11][15][16]. For this, Ni nitrate Ni $(NO_3)_2.6H_2O$ salt was mixed with citric acid (1:3) and then ethylene glycol was added (2:3 mol/mol of ethylene glycol and citric acid, respectively). The solution was kept at ~80 ^{0}C under mechanical stirring for about 4 h till the formation of a gel (after the removal of water through evaporation). Then, the obtained gel was dried in oven at 200 ^{0}C for 24 h. At this point, two approaches were followed. On one side, a specific mass of NiO nanoparticles precursor powder for obtaining a final loading of 15 wt. % Ni (determined by performing a TGA-DSC analysis of the precursor powder) was calcined in presence of the corresponding mass of Cs-USY zeolite under air flow 500 °C for 6 h. This process was named as co-calcination (CC). On the other side, the NiO nanoparticles precursor powder was calcined in muffle at 500 °C for 6 h and then the resulting NiO nanoparticles were mechanical mixed (MM) and impregnated (IWI, using a TMAOH 1 M solution) over the corresponding Cs-USY mass in order to obtain 15 wt.% Ni catalysts.

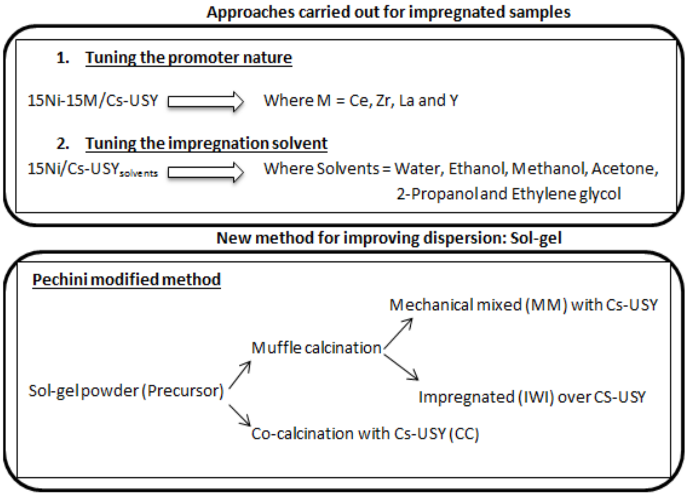

Figure 1: Strategies followed for tuning Ni particle size.

2.2. Catalysts characterization

All prepared catalysts were characterized by thermo-gravimetric analysis (TGA), X-ray diffraction (XRD) and temperature programmed reduction with hydrogen (H_2-TPR).

Thermogravimetric analysis (TGA) allows monitoring mass variations in a material as a function of temperature while a controlled temperature program is running. In this work a Setsys Evolution TGA from Setaram instruments was used to perform TGA-DSC analysis. For each experiment, a mass of catalyst around 30 mg was used. A heat treatment was applied from 20 to 400 °C using a rate of 10 °C/min and a gas (air in all cases except for sol-gel samples, where nitrogen was used) flow of 30 ml min^{-1}. This heat treatment was done twice in a manner that result from the second cycle were subtracted in the first cycle to eliminate the possible error or noise.

Powder XRD patterns were obtained in a Bruker AXS Advance D8 diffractometer equipped with a 1D detector (SSD 160) and using a Ni filter for identifying crystalline phases. The scanning range was set from 5° to 80 ° (2θ), with a step size of 0.03° and a step time of 0.5 s. In this work, powder X-ray diffraction was used to get information about the types of phases present on the prepared catalysts and to estimate average NiO/Ni^0 sizes through Scherrer equation.

H_2-TPR tests were carried out in a Micromeritics AutoChem II using around 0.150 g of catalyst in every experience. At first, catalysts were pre-treated under argon flow (25 ml min^{-1}) at 250 ^{0}C for 1 h, with a ramp of 10 °C/min, and then cooled down to the room temperature. Then, TPR was carried out by flowing 30 ml min^{-1} of a 5%H_2/Ar flow and raising the temperature from room temperature to 900 °C, at 10 °C/min. In these experiments, samples were placed in a reducing atmosphere and H_2 is circulated through the catalyst bed while the temperature is varied linearly. H_2 consumption as a function of temperature was continuously monitored through TCD detectors.

2.3. Catalytic Tests

The catalytic tests were carried out in a Pyrex reactor under atmospheric pressure. The reactor was heated in a TermoLab electric oven, using a temperature controller, and a thermocouple was placed inside the reactor close to the catalytic bed to follow the variation of the temperature of the sample during the tests. All Gases (N_2, H_2, and CO_2) were supplied by Air Liquid with purities above 99.999% and regulated using mass flow controllers supplied by Brooks. Catalytic tests were performed using a fixed mass of catalyst (0.200 g) at atmospheric pressure. In-situ pre-reduction was generally performed at 470 ^{0}C for 1 h (heating rate of 2.5 ^{0}C min^{-1}) with 80%H_2/20%N_2 flow of 250 ml min^{-1} to get metallic Ni^0 species. In some specific cases (e.g. 15% Ni/Cs-$USY_{2\text{-}Propanol}$ and sol-gel catalysts) the effect of the pre-reduction conditions were evaluated. Indeed, for 15% Ni/Cs-$USY_{2\text{-}Propanol}$ a test was performed after reducing at 650 °C to evaluate the effect of this parameter in the amount of reduced metallic species, average particle size and catalytic performances obtained while, in case of sol-gel samples, tests were performed with and without in-situ pre-reduction. Catalytic tests were performed between 250 and 450 ^{0}C keeping a reaction feed gas of H_2, CO_2 and N_2 at a molar ratio of 36:9:10 (stoichiometric ratio between H_2 and CO_2, total flow = 290 ml min^{-1}). For each reaction temperature, after stabilization of catalytic system average value of the required data was taken for calculation of CO_2 conversion and CH_4 methane selectivity.

3. Results and discussion

3.1. Promoter nature effect (15Ni-15M/Cs-USY samples)

Firstly, **thermo-gravimetric analysis (TGA)** was performed for all samples from this study after saturation with water to check the strength of the water-zeolites interactions through h index calculation. Results revealed that the nature of the added promoter does not significantly affect the hydrophobic properties of the materials. Indeed, h indexes close to 0.80 were obtained for the different catalysts from the present chapter, being these values in accordance with the obtained in the literature for similar samples [17].

To follow the study, **XRD diffractograms** were collected for all the samples from this study and for comparison purposes, Cs-USY zeolite support pattern was also collected. All the samples showed the characteristic peaks of Faujasite (FAU) structure in range of 2θ = 5-45^o, characterized by the main diffraction peaks at 2θ = 6.4^o, 15.8^o and 23.7^o [18]. However, the zeolite peaks intensity decreased with the incorporation of the metals, which could be due to the formation of some amorphous phases after the metal loading or even due to the adsorption of X-rays by the promoter species incorporated. Moreover, characteristics peaks of NiO phases (2θ = 37 ^{o}, 43 ^{o} and 63^o) [19] and metallic nickel phases (2θ = 44.5, 51.8, 76.3^o) [20][19] were observed in calcined and reduced samples respectively. Additionally, no peaks attributed to Ce oxides, Zr oxides, La oxides, nor Y oxides were found in the respective samples, what could be ascribed to a high dispersion of the metal promoters over the structure. Particle sizes varied following the order: Ni-Ce (<5 nm) < Ni-Y (9 nm) < Ni-Zr (24 nm) < Ni-La (27 nm).

H_2-TPR experiments were carried out (Figure 2). For comparison purposes, the profile obtained for the equivalent monometallic sample (15%Ni/Cs-USY_{Water}) was also obtained. To be pointed out is that, in samples with Y and Ce, a great fraction of NiO species was observed to be present in the cavities of zeolites due to presence of highly dispersed metal oxides phases as verified with XRD results. Additionally, temperature shifts on the peaks maxima with respect to the monometallic sample (15%Ni/Cs-USY_{Water}) can be observed with the incorporation of some promoters (e.g. Ce, Y), suggesting the establishment of synergistic interactions between Ni and the promoters, which create new levels of metallic interactions. However, in the catalysts with Zr and La, not such remarkable differences can be observed, which could indicate that the addition of these promoters does not modify significantly NiO species reducibility.

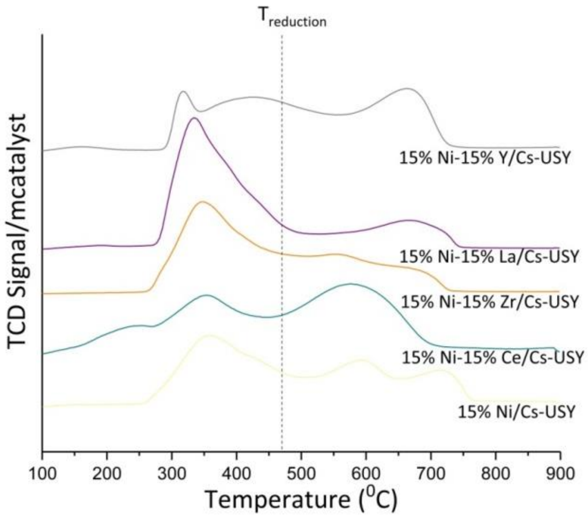

Figure 2: H_2-TPR profiles of promoted samples.

Catalytic performances results showed that the un-promoted 15% Ni/Cs-USY$_{Water}$ catalyst exhibits generally lower CO_2 conversion and selectivity than the bimetallic catalysts. In order to clearly study the effects of the different promoters to the activity of the materials towards carbon dioxide methanation, methane yields determined for the bimetallic samples at three representative temperatures are depicted in Figure 3. Thus, it can be seen that results followed the trend: Ni-Y > Ni-Ce > Ni-La >> Ni-Zr. As seen, yttrium remains as the most favorable promotor, followed by cerium, which could be due to the favored particle sizes (Ni^0) as verified with XRD characterization and the enhanced reducibility of NiO species [21][22], without excluding a possible effect of Y in the number of CO_2 activation sites.

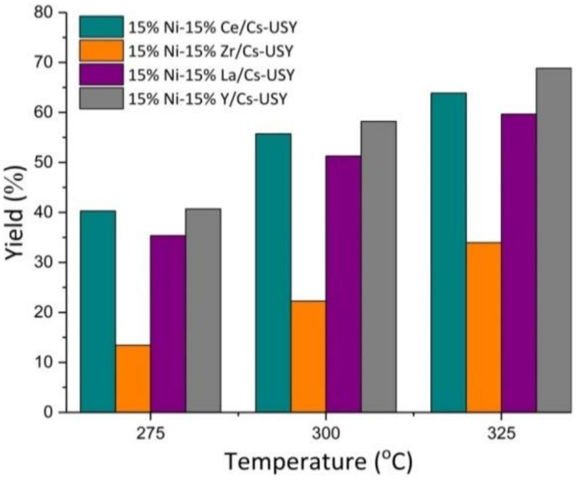

Figure 3: Methane yield of different promoted catalysts.

3.2. Impregnation solvent effect (15Ni/Cs-USY samples)

As done for the bimetallic samples, **thermo-gravimetric analysis (TGA)** was performed for the catalysts from this study after saturation with water. Results revealed that, the nature of the impregnation solvent does not lead to significant changes in the hydrophobic properties of the materials, with h indexes of ~0.95 in all samples. Thus, the strong hydrophobic nature of the zeolite support seems to be preserved.

Regarding **XRD patterns** obtained, zeolite structure was still preserved irrespective of the solvent used with the exception of ethylene glycol sample, where zeolite characteristic peaks intensity significantly decreased with the thermal treatments, indicating the damage of the structure as verified from sample crystallinities. Moreover, characteristic peaks of Ni phases were also found present. According to the obtained results, 2-propanol and ethylene glycol samples presented the smallest Ni^0 particles (13 nm), followed by methanol (17 nm), water (19 nm), ethanol (21 nm) and acetone (22 nm). To be remarked is that, while for most of the samples the variation between the NiO and Ni^0 sizes is similar (2-4 nm), in the ethylene glycol sample the occurrence of severe sintering processes during the pre-reduction treatment is evident as the particle size doubles.

Regarding **H_2-TPR profiles**, the nature of the impregnation solvent used presented an impact in the reducibility properties of the synthesized catalysts. Indeed, samples with smaller NiO particles (2-propanol, ethylene glycol) present greater reduction processes at 550-750 °C (Figure 4). This behavior was somehow expected as the smaller particles could be easily located inside the cavities present in the zeolite, while agglomerated NiO particles will tend to be located in the external surface.

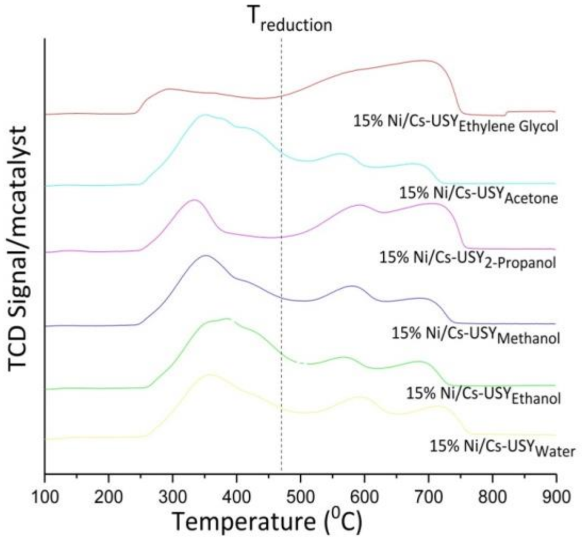

Figure 4: H_2-TPR profiles of samples with different impregnation solvents.

The catalyst presenting the better performances was the one prepared using 2-propanol as solvent, followed by ethylene glycol and then catalysts impregnated with water, methanol, ethanol and acetone. These findings were generally in well accordance with their XRD results in terms of Ni^0 particle sizes. In order to have clearer picture of catalytic performances for the samples prepared with different solvents, a bar graph presenting methane yields of the samples at three representative temperatures is presented in Figure 5. It can be clearly seen that the highest methane yield was provided by the use of 2-propanol. However, the results of ethylene glycol were lower than the expected when analyzing the particle size and reducibility of Ni species in this catalyst. Indeed, one can explain these unexpected results by the structural damage produced in the zeolite during the pre-reduction treatment, according to the crystallinity.

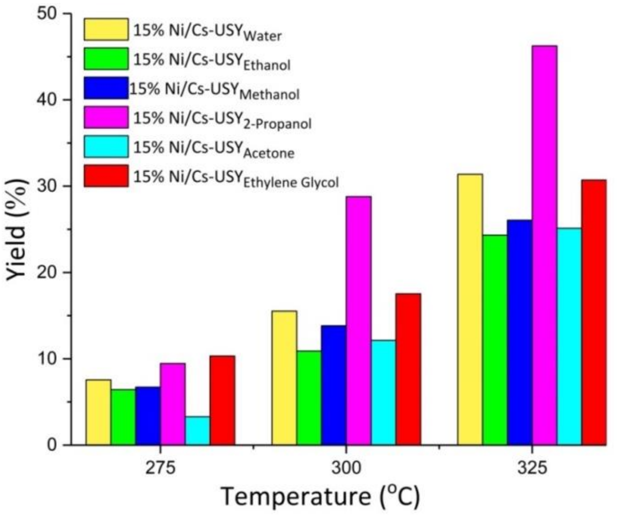

Figure 5: Methane yield of different impregnated catalyst.

3.3. New preparation method (Sol-gel)

Characterization results from **thermo-gravimetric analysis (TGA)** showed that the sol-gel materials presented similar hydrophobic properties, which were directly related with the zeolite support (h index and mass losses) as the pure nickel nanoparticles did not adsorb any water.

The **XRD patterns** obtained for the samples from this chapter after calcination and reduction revealed the coexistence of NiO and Ni^0 species in the samples prior to the reduction treatment (Figure 6), a fact not verified in any of the previous materials from this work.

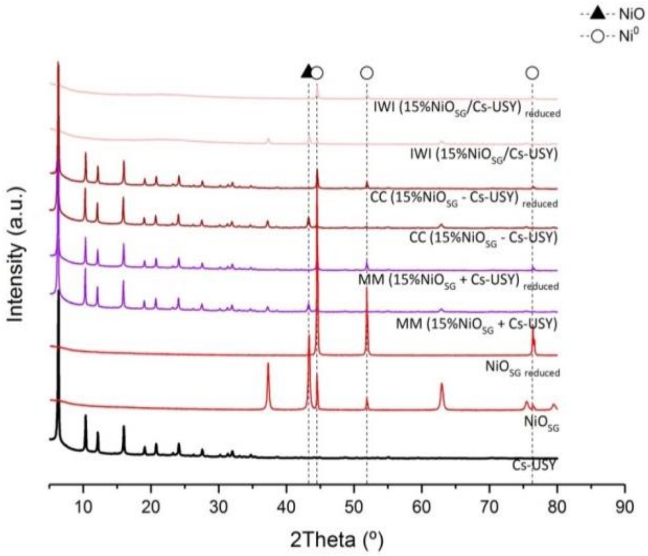

Figure 6: XRD of the Sol-gel samples and Cs-USY.

Indeed, whatever the preparation strategy followed in these sol-gel materials, all samples presented the characteristic diffraction peaks of NiO and Ni^0 after calcination and Ni^0 after reduction and also FAU structure was found preserved. However, the catalyst prepared by incipient wetness impregnation (IWI) using a TMAOH 1 M solution (for avoiding the agglomeration of the nickel nanoparticles and favoring the formation of a suspension) led to a severe damage in the zeolite, as no peaks can be found in the 5-40 ° region which could be due to highly basic nature of used solvent (TMA) resulted in solubility of silica species and hence damage to FAU structure [23].

Regarding **H_2-TPR profiles**, as observed that the samples prepared by sol-gel method presented a unique and prominent reduction process below 500 ^{0}C, indicating that the majority of Ni nanoparticles are present on the external surface of the zeolite support, with weak metallic-support interactions and probably more prone to sintering issues at higher temperature. According to the H_2 consumptions registered, only 20% of nickel species were presented as NiO in all sol-gel fresh samples (not submitted to any pre-reduction treatment). Consequently, it can be concluded that this preparation method leads mainly (approx. 80%) to the formation of Ni^0 nanoparticles.

As observed from Figure 7, the activity of the different materials follows, irrespective of the presence of a pre-treatment (pre-reduction), the order: NiO_{SG} > IWI > CC > MM. Considerably higher performances were observed for the unsupported nanoparticles as expected, since the number of Ni active sites was greater in this test (the mass of catalyst per test was kept constant) with 100 % Ni species in the total sample mass as compared to the other catalysts, which present 15 wt. % Ni and 85% of Cs-based USY support Regarding selectivity to methane, results followed the trend: NiO_{SG} > IWI > CC > MM. Anyway, the performances of the sol-gel materials were considerably lower than those reported for impregnated samples in previous chapters.

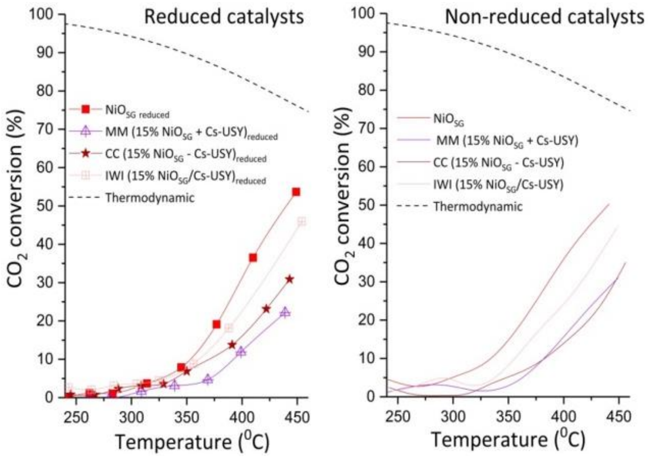

Figure 7: CO_2 conversion of sol- gel catalyst (reduced vs. non-reduced).

In order to properly compare the different samples in terms of Ni active sites per test, samples performances were depicted per gram of Ni in Figure 8, being observed that catalysts with 15 wt. % Ni interacting with zeolite support presented better methane yields than the unsupported NiO_{SG} catalyst. This confirms that the presence of a support promotes the metal-support interactions and is beneficial for the methanation activity and selectivity, in accordance with the literature [4].

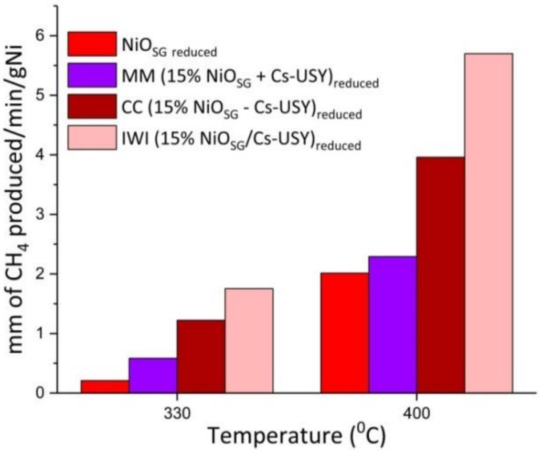

Figure 8: Methane yield of sol-gel catalyst over specific temperature (in tests with reduction treatment).

4. Conclusions

Power-to-gas constitutes a promising technology for storing the renewable electricity surplus produced in low consumption periods into synthetic natural gas. CO_2 methanation to produce synthetic natural gas (SNG) is typically carried out by using heterogeneous catalysis and, among all the reported materials, Ni-based zeolites have shown potential for this reaction. However, they present limitations in terms of Ni particles average sizes, being mandatory to explore strategies for improving metallic dispersion. To overcome with this problem three approaches have been developed for obtaining enhanced dispersion on Ni-based Cs-USY zeolites for application in CO_2 methanation in this work. Results verified that in among bimetallic catalysts yttrium led to the highest enhancement of the catalytic performances. Among all the studied solvents, 2-propanol was the one leading to the best performances both in terms of CO_2 conversion and CH_4 selectivity. Finally, regarding the study of sol-gel as preparation method, it was found that considerably larger Ni^0/NiO particles were formed by this strategy (30-50 nm), what justifies the low activities revealed by these samples However, confirming that using a supported catalyst rather than the pure Ni nanoparticles is more suitable. Taking into account the main results and conclusions resulting from the present work, future work could be suggested in order to complement the present study. Indeed, the characterization of samples interaction with CO_2 (e.g. CO_2-TPD, CO_2 adsorption followed by Operando FTIR), the study of the dispersion of Ni particles over the different materials by TEM and/or mapping and the preparation of a 15%Ni-15%Y/Cs-USY zeolite using 2-propanol as solvent could be performed in the future.

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