

NEW APPROACH TO THE PREPARATION OF ZEOLITE-BASED CATALYSTS FOR CO₂ METHANATION

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October, 2020

Abstract

In today's scenario, biomethane, has increasingly grown popular worldwide as one of the foremost technologies for producing renewable energy from different biomass sources. Biomethane can be obtained from the purification of the biogas produced by the anaerobic fermentation of organic waste (30-60 wt.% CO₂ and 40-70 wt.% CH₄). Biogas upgrading is carried out by separating CO₂ from CH₄ through adsorption, absorption or even membrane processes. An alternative strategy is the valorization of biogas through CO₂ methanation reaction. For that suitable CO₂ methanation catalysts need to be developed, and in literature, zeolites constitute promising support materials.

This work studied the preparation of metal-based (Ni, Ru) zeolite (HUSY, CsUSY) catalysts by solvothermal method. Firstly, the optimization of metallic nickel nanoparticles obtained by this method was performed. The effects of PVP/Ni wt. ratio, reaction time and different precursor salts were investigated. Samples were characterized by X-ray diffraction, temperature programmed reduction (H₂-TPR) and nitrogen physisorption. CO₂ methanation performances were evaluated in a laboratory-scale unit under experimental conditions previous optimized.

The best conditions to obtained NiO nanoparticles with sizes < 20 nm were using a PVP/Ni ratio = 5 and reaction time of 12 h. However, these conditions induced the destruction of the zeolite structure, which explained their catalytic performances, lower than those exhibited by equivalent catalysts prepared by impregnation method. Among all, CsUSY zeolite supported catalysts led to the best catalytic performance.

Keywords: Biogas upgrading, CO₂ methanation, Zeolite catalysts, Solvothermal method.

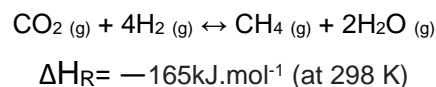
1. Introduction

The world's energy demand has been increasing over the years with fossil fuels being the major source of energy in the past years. Decades ago, the OECD countries made up for most of the consumption of energy in the world however, due to the increasing population, economic growth and increase in the standard of living in the Non-OECD countries, mostly India and countries in Africa in the coming years, energy consumption would still be on the rise [1]. The vast majority of the world's energy supply comes from fossil fuels such as coal, oil and natural gas with nuclear and renewable energy sources joining the mix in the 1960s and 1970s respectively [2]. However, due to the rise in GHG emissions associated with the energy use, the world came together under The Paris Agreement to limit the global warming temperature below 2 °C and further to 1.5 °C [3]. One of the mitigation strategies which can be employed towards reducing emissions is the use of renewable energy sources for decarbonisation of the energy sector. Renewable energy sources produce much lower emissions, increase energy security and access; social and economic development [4].

Among the different renewable energy sources, biomass seems to have an edge over others as it competes most favorably in all countries of the world. Biomass energy is considered a renewable and sustainable energy source and has attracted much attention at global and national levels [5]. Biomass can be combusted directly to produce energy and can also be used as feedstock to produce a variety of liquid or gas fuels (biofuels). Anaerobic digestion is a biological process of breaking down organic matter (in this case

biomass) in the absence of oxygen to produce digestates and biogas, which consists mainly of methane and carbon dioxide with some traces of nitrogen and hydrogen sulfide, among all [6], [7]. The yield and composition of biogas is affected by the type of raw material used in the production process. The typical composition of raw biogas from anaerobic digestion is 45-70% of CH₄, 30-55% of CO₂, 0-5% of O₂ [8].

Biogas upgrading to biomethane is based on the removal of CO₂. However, with technological advancement in the world today, perhaps there is a better alternative which can further explore the value of a raw biogas. To exploit the large amount of CO₂ content in biogas, there is a proposed method for increasing the biomethane yield which is by direct catalytic conversion of CO₂ into biomethane through methanation (Sabatier reaction) using hydrogen produced from RE sources (shown in chemical reaction below).



The typical catalysts used for the CO₂ methanation reaction have metal-based materials (e.g. nickel, cobalt, ruthenium, rhodium) added to a support [9]. Possible mechanism for CO₂ methanation is represented in Figure 1 [10].

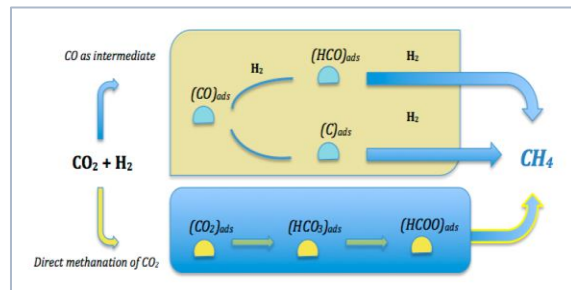


Figure 1: Mechanism of CO₂ Methanation Reaction [10].

Noble and transition metals supported over different materials are the most studied catalysts for the CO₂ methanation reaction [11], [12].

Although ruthenium and rhodium have shown higher performances than nickel, most studies remain focused on improving the activity, selectivity and stability of Ni-based catalysts due to its lower cost and availability [13]. Ruthenium is one of the most active catalysts for methanation process [10], [14], [15]. Its catalytic activity highly depends on the dispersion of the metallic phase, type of support and presence of promoters or modifiers. Ru catalysts are known to be highly stable over a wide range of temperature and also very highly active towards methanation process, but fairly expensive [15], [16]. Additionally, nickel catalysts are the most studied for CO₂ methanation because of their high efficiency, availability and low cost. According to [10], [14], [17], the effect of using different supports (α -Al₂O₃, MgO, TiO₂, and CeO₂) in the preparation of Ni catalysts has been studied. Morphology of the active sites, adsorption ability and improving the catalytic features are the essential qualities of supports for effective methanation process [9]. Zeolites, crystalline aluminosilicates with suitable chemical and textural properties for the methanation reaction, are among the possible supports that can be used for the catalysts [14], [15].

Zeolite-supported catalysts have revealed promising results, especially due to their tunable properties in terms of basicity and hydrophobicity to satisfy the characteristics necessary to achieve active, stable and selective materials for CO₂ methanation [18]. However, their main drawback arises from the relatively large Ni⁰ particles (25-30 nm) formed in absence of promoters. Thus, looking for new synthesis methodologies that allow the formation of smaller Ni⁰ particles over

zeolite supports is mandatory. For these reasons, the objective of this work was to analyze a new approach to the preparation of zeolite-based catalyst for CO₂ methanation process: using the solvothermal method. To the best of our knowledge, this approach has not been tried before, representing a challenging and innovative strategy. The factors influencing the catalyst's synthesis were investigated to determine optimal preparation routes. Ni and Ru-based USY zeolites were synthesized, characterized and finally tested under CO₂ methanation conditions.

2. Experimental

Preparation of metallic Ni nanoparticles: the preparation was carried out by the solvothermal method, a common procedure to synthesize inorganic nanoparticles (NPs). This method was used for the preparation of metallic Ni NPs and also to Ni or Ru/Zeolite catalysts. For metallic Ni NPs synthesis, the feed components, including Ni precursor, ethylene glycol (used as reducing agent for the metallic ions), PVP ([C₆H₉(NO)_n], molecular weight = 40 000, used as a nucleation-protective agent to avoid nanoparticles sintering and agglomeration) and NaOH pellets (used to adjust the pH value to ca. 12), were mixed together in predefined proportions. The obtained solution was then thoroughly mixed using a magnetic mixer until it became homogenous. The nickel salt (precursor) concentration was 0.05 M in the solution and, for the synthesis that included zeolites as support, the nominal composition of Ni was calculated to obtain 15 wt.%. Afterwards, the solution was placed in an autoclave and heated at 180 °C (with an increase of 10°C per minute) to reduce the Ni ions and form to metallic Ni. Consequently, the product obtained was allowed

to cool down to room temperature. There was an observation in the change of color for the solution, which indicates nucleation and growth. The obtained product was then centrifuged with excess ethanol at 2750 rpm for 5 min in a centrifuge. This process was repeated for approximately 3-5 times for the liquid to be properly separated from precipitate. Once the centrifugation process was completed, the product was further dried in a vacuum system installation at 70 °C using liquid nitrogen.

Preparation of Ni-Zeolite Catalysts: a USY zeolite provided by Zeolyst with a Si/Al ratio of 38 (CBV 780) has been used as support both in commercial (HUSY) and Cs-exchanged (CsUSY) forms, previous prepared. For the preparation of Ni/zeolite catalysts, the Ni precursor selected was nickel chloride, for the preparation of Ru/zeolite catalysts, the Ru precursor chosen was ruthenium chloride. The preparation conditions are similar to that of Ni except the reaction time of 12hrs. Furthermore, the nominal composition of Ru was calculated to obtain 3 wt.%.

Characterization of the catalysts: Powder X-ray diffraction for Ni- and Ru-Zeolites was carried out in a Bruker AXS Advance D8 diffractometer equipped with a 1D detector (SSD 160) and using a Ni filter. The scanning range was set from 5 to 80 ° (2 θ), with a step size of 0.03 ° and a step time of 0.5 s. H₂-TPR measurements were carried out in a Micromeritics AutoChem II using around 0.150 g of catalyst in every experiment. Catalysts were pre-treated under argon flow (25 ml min⁻¹) at 250 °C, with a ramp of 10 °C/min and then cooled down to the room temperature. Then, H₂-TPR was carried out by flowing 30 ml min⁻¹ of a

5%H₂/Ar flow and raising the temperature from room temperature to 900 °C, at 10 °C/min.

N₂ physisorption was used to obtain the specific surface areas of catalysts samples with support by Brunauer-Emmett-Teller method (equation is found below [19]) and the measurements were carried out using a Micromeritics ChemiSorb 2720 – ChemiSoft TPx system. The samples were subjected to a flux of 30%N₂/He (P/P₀=0.3) at 20mL/min. The surface area was calculated based on the desorption peaks using the Micromeritics software installed.

CO₂ methanation measurements: 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 °C for 1 h (heating rate of 5 °C.min⁻¹) with 80%H₂/20%N₂ flow of 250 ml min⁻¹ to get metallic Ni⁰ species. In the case of mechanical mixtures composed by CsUSY zeolite and Ni⁰ NPs, no pre-reduction was carried out. Temperatures between 250 and 450 °C were studied, keeping a reaction feed gas of H₂, CO₂ and N₂ at a molar ratio of 36:9:10 (stoichiometric ratio between H₂ and CO₂, 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 CO₂ conversion and CH₄ methane selectivity.

3. Results

Effect of PVP/Ni ratio

Figure 2 shows the XRD pattern of the synthesized Ni NP samples with varying PVP/Ni and at 20 h of reaction time. There are three diffraction peaks observed from the graph with 2 θ values of 44.5°, 52.1° and 76.5° that corresponds to metallic Ni NPs (JCPDS card no. 04-850) [67].

Unfortunately, sample 0PVP/Ni_{20h} showed an additional diffraction peak with 2θ values of 47.2° which corresponds to silicon (Si) (JCPDS no. 27-1402) [66]. The detection of Si in the XRD pattern can be explained as a result of the sample holder's problem during the XRD analysis [20].

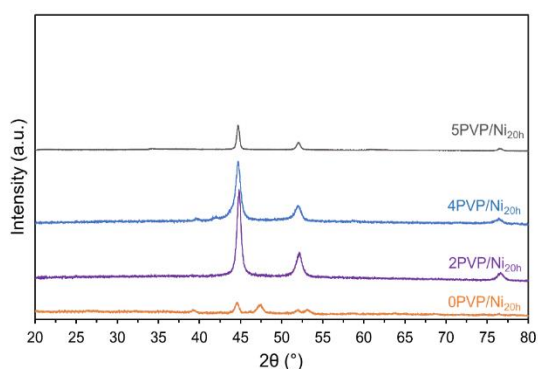


Figure 2: XRD patterns for 20 h reaction time Ni NP samples.

Furthermore, XRD analysis data was used to estimate the average nickel nanoparticle sizes by applying Scherrer's law (using the maximum intensity peak that corresponds to 2θ values of 44.5°, *hkl* 111). As expected [21], it was observed that there is a decreased in particle sizes as the PVP/Ni ratio increases up to 4. At PVP/Ni 5, an increase in the particle size is noted. This can be attributed to the possibility of sintering of the NPs sample in the autoclave causing the particle size to increase.

Effect of reaction time

The XRD patterns obtained confirm the presence of mainly Ni⁰. No other significant peak diffraction peaks were observed. As previously done, average particle sizes were determined (Figure 3). At higher reaction times the particle sizes were similar, with no tangible difference between them. This result led to the conclusion that reaction times do not lead to a significant impact on the NPs size.

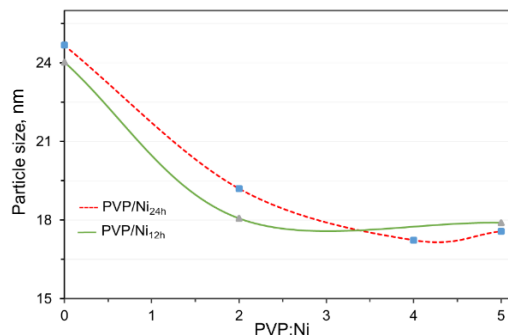


Figure 3: Graph of NP sizes against PVP/Ni ratio with reaction time of 12 and 24 h. (PVP/Ni - wt. ratio)

Effect of Nickel salt

Different Ni precursors were used to synthesize the Ni NPs to study and analyze how they affect the particle sizes of the NPs. The XRD analysis of the NP samples with various precursors is shown in Figure 4. It can be seen that all diffractograms present the characteristic peaks for Ni⁰ phase. The major difference noticed between the precursors is the intensity of the peaks, related with the average particle sizes obtained. Indeed, an increase in particle size reduces the broadness of the peak which could translate to a nonuniform dispersion if incorporated on a support.

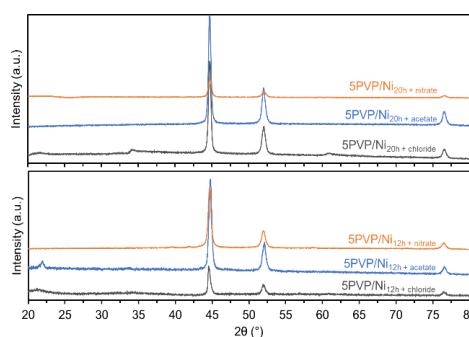


Figure 4: XRD patterns for Ni NP samples with different precursors at 12 and 20 h reaction time.

Overall, considering the results obtained, a conclusion was reached based on the above analyzed key-points and the most suitable conditions to further study the process for the

synthesis of Ni-based catalysts over zeolite supports were selected to be the following: i) PVP/Ni wt. ratio: 5; ii) Reaction time: 12 h and 20 h (at 180 °C). and iii) Precursor salt: NiCl₂.

Catalytic performance of the supported catalysts

To start, four Ni/USY catalysts were synthesized using 12 and 20 h of reaction time and two types of zeolites with variable compensating cations: H⁺ (HUSY, acidic and hydrophilic zeolite) and Cs⁺ (CsUSY, more basic and hydrophobic zeolite). The XRD patterns of the Ni/USY catalyst samples are shown in Figure 5. As noticed, it can be seen that there are no intense nor clear peaks in the diffractogram, which suggests that the metal species could be highly dispersed in the zeolite. Complementary, the lack of zeolite characteristic peaks in the metal-containing catalysts indicates the destruction of the zeolite structure [22].

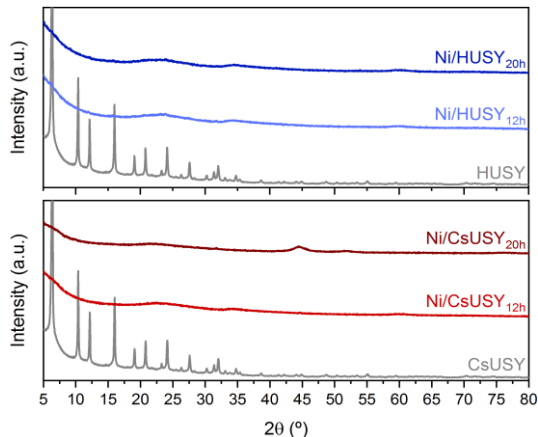


Figure 5: XRD pattern of Ni/USY catalyst samples prepared at 12 and 20 h reaction time

Regarding the BET surface area of the catalysts (S_{BET}) discussed above, compared to the zeolites, the S_{BET} surface of catalyst samples were significantly lower (9 m²/g for Ni/HUSY12h and 20h, 60 m²/g for Ni/CsUSY12h and 13 m²/g for Ni/CsUSY20h) than those found for the HUSY (450 m²/g) and CsUSY (579 m²/g) supports,

which could be due to the damage of the zeolite structure and/or to the presence of precursor salt in the samples.

To further investigate, the catalyst samples prepared at 12 h reaction was characterized by H₂-TPR (Figure 6). As verified, negative peaks were revealed by both catalysts, which confirm the earlier hypothesis regarding the presence of a part of the precursor salt remaining in the samples even after the synthesis procedure, considering that any heat treatment was performed.

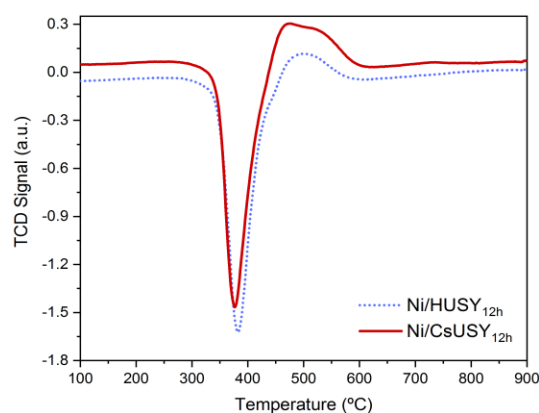


Figure 6: H₂-TPR profiles of Ni/USY catalysts at 12 h reaction time.

Furthermore, in terms of catalytic performances, CO₂ conversion and CH₄ selectivity, are presented in Figure 7. Analyzing the effect of reaction time, lower activities were observed for the catalysts prepared at 20 h as compared with 12 h reaction time in both the HUSY and CsUSY supported catalysts. This effect could be ascribed to the formation of larger Ni particle. However, there is a more pronounced difference between the activities of Ni/HUSY catalyst samples, an effect that could be related to the nature of the zeolite. Indeed, in the literature it was reported that Ni/USY zeolites containing larger compensating cations (Cs⁺) can partially

suppress metal agglomeration processes, increasing the resistance towards sintering [23]. Considering that H₂-TPR revealed that part of the precursor salt might be present in the samples, the best materials (Ni/HUSY_{12h} and Ni/CsUSY_{12h}) were calcined in a muffle for 2 h at 500 °C using a heating rate of 1 °C/min under atmospheric air.

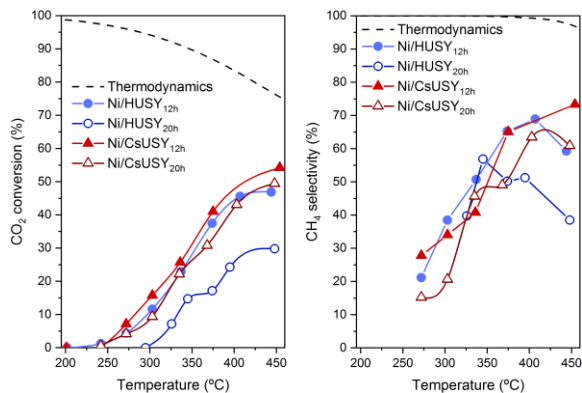


Figure 7: CO₂ conversion and CH₄ selectivity vs. temperature, at GHSV = 43 000 h⁻¹ for the Ni/USY catalysts. Dashed line – thermodynamic equilibrium conversion values.

It was expected that the calcination treatment will help to convert any remaining precursor salts on the support into NiO. Calcined samples present mainly reduction processes below 650 °C (Figure 8), which might be ascribed to the reduction of NiO species formed over the materials. The reducibility was clearly influenced by the nature of the zeolite support, with the HUSY leading to stronger Ni-support interactions.

Catalytic tests were run over the calcined materials. CO₂ conversions and CH₄ selectivity were higher in the uncalcined samples. This unexpected behavior could be related to the negative effect of carrying out two thermal treatments at high temperature (calcination at 500 °C) in the agglomeration of Ni particles for the case of the calcined samples.

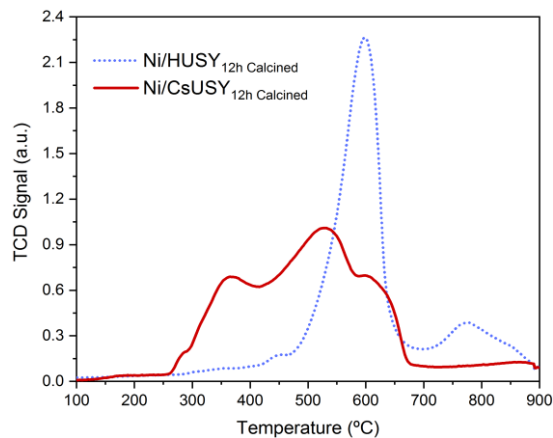


Figure 8: H₂-TPR profiles of calcined Ni/USY catalysts at 12 h reaction time.

In order to verify the best type of zeolite support, CH₄ yields were determined (Figure 9).

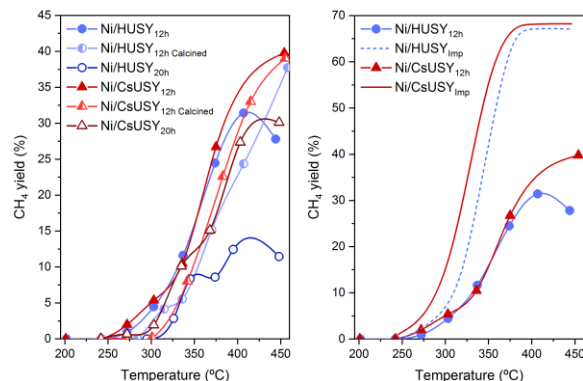


Figure 9: Comparison of different catalyst samples on the CH₄ yield in temperature range 200–450 °C.

As shown on the graph, at the specific reaction conditions used, the CH₄ yield was highly far from the equilibrium points for all the solvothermal samples. The yield of CH₄ for the catalyst samples mostly occurred from temperature above 300 °C and the highest CH₄ yields were obtained at above 400 °C. Catalyst prepared at solvothermal 20 h had the lowest CH₄ yield, this may be due to the longer reaction time causing the sintering of the catalysts, carbon deposition on the catalyst's active sites [24] as well as reducing its surface area. Also, calcination did not favor in a significant manner the catalytic

performances, probably due to the promotion of Ni particles aggregation due to the two thermal treatments carried out prior to the test. Overall, CsUSY-based catalysts, namely Ni/CsUSY_{12h}, exhibited the most promising results.

Furthermore, Abu Bakar *et al.* [25] work suggested that catalyst's preparation method may have an impact on how metallic Ni NPs is dispersed on the support, Ni/HUSY_{12h} and Ni/CsUSY_{12h} catalysts results were compared with those obtained for reference catalysts prepared by incipient wetness impregnation method [26], [27]. As seen, impregnation samples led to a significantly higher CH₄ yield, which could be due to the fact that zeolite structure was preserved in the impregnated samples [27]. Moreover, with the objective of identifying the effect of the active metal nature, the best sample (Ni/CsUSY_{12h}), was compared to an equivalent Ru catalyst (Ru/CsUSY_{12h}).

Figure 10 shows the performance result. With Ni/CsUSY_{12h} catalyst, the CO₂ conversions are higher, while the use of Ru significantly favored CH₄ selectivity, in accordance with the other studies [17], [28].

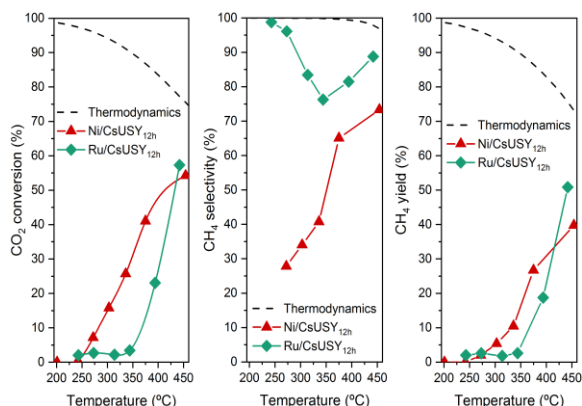


Figure 10: Comparison of the performance of Ru/CsUSY with Ni/CsUSY.

Complementary, the CH₄ yield over Ru/CsUSY_{12h} catalyst was higher than the obtained for the

Ni/CsUSY_{12h} above ~425 °C. These results indicate that Ru loading and pre-reduction temperature must be optimized in solvothermal Ru-samples, as the 3 wt.% Ru and 200 °C (best conditions) arising from impregnation studies could not be the most appropriate when changing the synthesis method.

4. Conclusion

CO₂ methanation can be considered as a promising alternative for upgrading biogas into biomethane as it allows the maximization of the renewable carbon valorization. Among the different methanation catalysts found in the literature, the use of zeolites has led to interesting results so far. However, the considerably large Ni⁰ particles obtained in absence of promoters (25-30 nm) and by conventional impregnation method are one of their main drawbacks.

In this context, the present research project aimed to investigate the preparation of Ni/USY catalysts by using solvothermal method, a low energy intensive process. The influence of the reaction time, PVP/Ni ratio and Ni metal precursor in the Ni NPs size were evaluated and properly optimized, in order to use the best conditions in the preparation of metal-based zeolite catalysts. As expected, using high PVP/Ni ratio allowed the formation of Ni⁰ particles with sizes lower than 20 nm while high reaction time did not significantly impact the NPs sizes. Complementary, the nature of the Ni precursor salt led to a slight impact in the results, when the samples prepared at 12 h were compared (reaction time) and a higher impact when the samples were prepared at 20h. Based on the results obtained, the most favorable conditions for the preparation of Ni and Ru-based USY

catalysts were established to be 12 and 20 h with PVP/Ni ratio of 5, using the chloride salts.

Regarding the zeolite-containing samples, the use of 12 h as reaction time was responsible for higher catalytic performances. Complementary, the choice of a basic and hydrophobic zeolite (CsUSY) was found as more promising. Despite the verified destruction of the zeolite structure during the synthesis procedure, probably due to the required addition of NaOH in the protocol for the pH adjustment, favorable metal-support interactions might be established during the solvothermal procedure, as mechanical mixtures of CsUSY and Ni NPs led to lower performances and evident metallic sintering. Finally, no improvements were verified when using Ru instead of Ni as active method, probably due to the differences in terms of metal loadings. Overall, solvothermal samples showed moderate potential towards CO₂ methanation, especially when comparing with equivalent samples prepared by impregnation method where the zeolite structure was preserved. However, the produced catalyst still requires tangible improvement to obtain significant CO₂ conversion and selectivity to CH₄.

On the other hand, the comparison of Ru-based catalyst, which is a very good active metal for methanation, with the Ni-based showed a slightly better result. The characterization of the Ru/CsUSY catalyst showed the presence of zeolite structure diffraction peaks which means the structure was unaffected as in the case of Ni/USY samples.

In conclusion, the results obtained in this work showed that further efforts must be done for improving the performances of Ni/zeolite

catalysts synthesized by solvothermal method. To optimize the synthesis process and achieve better results, this work should be extended to varying other parameters including % of Ni loading, different calcination temperature and use promoters in order to improve the metal particle size and dispersion as well as study their effect on catalytic behavior.

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