

Florence Bauer

Influence of Mg and Ce in Ni/USY zeolites on CO₂ methanation

Bachelor's project in Chemistry

Supervisor: Muhammad Mohsin Azim

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Kunnskap for en bedre verden

Abstract

The greenhouse gas CO_2 can be converted into CH_4 to reduce its concentration in the atmosphere.^[1] The Ni/USY zeolite can be used to catalyse the CO_2 methanation reaction.^[1;2] Research indicates that the catalyst effectiveness can be improved by the dispersion of metals such as Mg and Ce.^[2] Here the effects of Ni, Mg and Ce in Ni/USY on the CO_2 methanation reaction are analysed taking into consideration temperature, dispersion method and the concentration of the metals. At low temperatures a high Ni content (ca. 15%) and a high amount of impregnated Mg (9%) or Ce (7%) is beneficial for conversion, with Mg and Ce leading to similar conversion values. For higher temperatures reasonable conversion can be reached with low Ni concentrations and ion exchanged Mg or impregnated Ce with 1.4%Mg4.5%Ni/USY being the most promising catalyst. Alternatively, for higher temperatures a higher Ni content is useful, but the addition of Ce or Mg only increase the conversion by a few percent.

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1 Introduction

CO₂ is a strong contributor to global warming and reducing its concentration in the atmosphere has become an important field of research.^[1] CO₂ emissions and the high CO₂ concentrations in the atmosphere can be reduced by using renewable fuels, storing CO₂ or through CO₂ conversion.^[1] CO₂ conversion appears promising as this greenhouse gas can be converted into useful industrial materials.^[1] One CO₂ conversion methods is catalytic hydrogenation which can lead to formation of products, such as CO, CH₄ or CH₃OH.^[1] Conversion of CO₂ into methane is useful as the synthetic CH₄ can be used for domestic and industrial purposes.^[3;4] The CO₂ methanation reaction is given by



This reaction is usually catalysed through heterogeneous catalysts, using different oxides or metals.^[5] Research indicates that Ni-based catalysts are well suited for industry considering its very effective for CO₂ methanation and Ni is a comparatively cheap metal relative to other catalysts.^[1] Additionally, zeolites, having a highly porous structure creating large surface areas available for catalysis are considered excellent catalyst.^[6;2] Zeolites can stabilize metals and lead to a favorable metallic dispersion due to their strong metal-surface interaction.^[7] Specifically USY zeolites appear promising as catalysts for CO₂ methanation.^[2] Consequently, research on USY zeolites with incorporated Ni is interesting to pursue with respect to improving CO₂ methanation catalysis.

Two factors need to be taken into consideration when evaluating Ni/USY zeolites as catalysts for CO₂ methanation. Firstly, sintering in Ni/USY is a problem as it leads to blocked pores, decreasing the catalysts effectiveness.^[2;8;9] Secondly, the reaction temperature necessary for obtaining satisfactory CO₂ conversion yield should not be too high. To increase the Ni/USY zeolite catalyst effectiveness, reduce reaction temperatures and decrease Ni sintering for CO₂ methanation, other metals can be added to the zeolite.^[2] Literature indicates that Mg and Ce are suitable metals as compared to other cations as they have the strongest influence on the Ni/USY catalyst effectiveness.^[2;10]

Considering the benefits of zeolites containing Ni for CO₂ methanation this project aims to analyse Ni/USY zeolites with Ni concentrations of around 5 and 15% and deduce conditions which can improve the conversion reached by the zeolites. Specifically, the effects of adding Mg and Ce will be looked at. Factors such as the temperature, amount of additional cations (Mg and Ce) and dispersion method will be taken into account.

2 Theory

Zeolites are microporous crystalline structures made of aluminium, silicon and oxygen.^[11] Pores in a structure increase the surface area for catalytic reactions to occur on meaning highly porous structures such as zeolites are excellent catalysts.^[6] In zeolites Si⁴⁺, Al³⁺ and O²⁻ form a three dimensional network in which Si and Al coordinate to four O atoms and each O coordinates to Si and/or Al atoms.^[12] In general, corner sharing TO₄ (Si or Al) tetrahedra construct zeolites where T refers to the tetrahedrally coordinated cation.^[13] The tetrahedra can bond in various ways forming different types of pores leading to the wide range of zeolite structures, also referred to as frameworks, with different properties.^[13] One example are sodalite cages, which consist of six 4 rings (made of 4 TO₄) and eight 6 rings (made of 6 TO₄).^[13] These sodalite cages construct various types of other frameworks such as SOD, LTA or FAU as shown in figure 2.3.^[13] The pore size and shape influence what molecules can enter the pores, react and diffuse out, and consequently influences the catalytic effect.^[2] Section 2.2 will go into more depth on the structures of zeolites, specifically Y and USY zeolites.

2.1 Zeolite acidity

In zeolites the trivalence of the aluminium leads to a negatively charged framework as the charges are not balanced out by surrounding atoms (see figure 2.1).^[12] The negative charge attracts cations, such as protons or metal cations which connect to the oxygen at the Si-O-Al bridge (see figure 2.1).^[11] Bonding protons lead to the zeolite developing Brønsted acid properties due to hydrogen's lower electronegativity relative to oxygen's.^[14] The hydrogens are consequently also referred to as Brønsted acid sites.^[15] The addition of metal cations leads to a similar acidic effect.^[15] The metal cations coordinate to the negatively charged oxygen which balances out the charge, however the metal cations still retain their positive charge

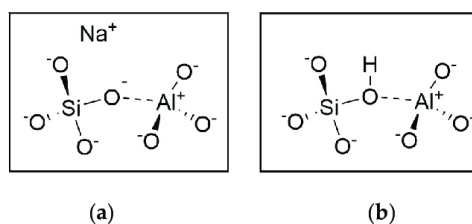


Figure 2.1: Bonding of silicon, oxygen and aluminium in zeolites and how this leads to a metal cation (Part (a)) or a proton (Part (b))balancing out the negative charge on the aluminium atom. Reprinted with permission from: Verdoliva, Valentina & Saviano, Michele & Luca, Stefania. (2019). *Zeolites as Acid/Basic Solid Catalysts: Recent Synthetic Developments*. Catalysts. 9. 248.

which results in the formation of an acidic site, also referred to as a Lewis acid site.^[16;15] These metal cations are also referred to as compensating cations.^[10] Through exploiting the different types of cations and their properties one can tune zeolites to have a certain acidity.^[14]

The acidic cations provide an adsorption site and can activate CO_2 molecules enabling them to react.^[17] The oxygen atoms on CO_2 act as nucleophiles and coordinate to the acidic metal cations (M^{n+}), this chemical adsorption is shown in figure 2.2.^[17;18] Multiple factors, such as the charge density, the coordination the cation has to the zeolite and the cation's position determine whether the cations lead to good adsorption of CO_2 molecules.^[19] Considering aluminium atoms are responsible for the acidic cations, a

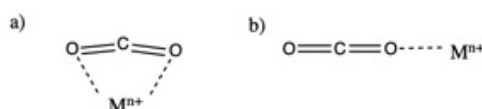


Figure 2.2: Two ways CO_2 can coordinate to metal cations. Image inspired by P.Tundo, L.He, E.Lokteva and C.Mota, *Chemistry Beyond Chlorine* Springer International Publishing, 2016

high amount of aluminium atoms relative to the silicon amount (meaning a low Si/Al ratio) leads to more CO_2 adsorption sites.^[2]

2.2 Y and USY zeolite framework

Y zeolites have a Si/Al ratio of 2.6 and a faujasite (FAU) type structure in which sodalite cages are coordinated to one another the same way carbon is bonded in a diamond structure.^[20;14] In the FAU structure sodalite cages combine through the tetrahedra in the 6-rings and form another larger three dimensional pore.^[20] This pore, also referred to as a supercage, consists of four 12-ring openings meaning 12 tetrahedra coordinated in a circle (see figure 2.3).^[13]

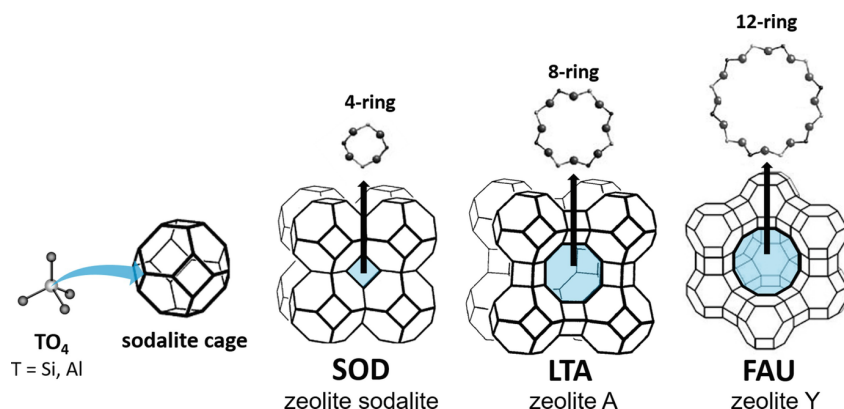


Figure 2.3: Sodalite cage and FAU structure. Reprinted with permission from Schwanke A.J., Balzer R., Pergher S. (2018) Degradation of Volatile Organic Compounds with Catalysts-Containing Zeolite and Ordered Mesoporous Silica. In: Martínez L., Kharissova O., Kharisov B. (eds) *Handbook of Ecomaterials*. Springer, Cham using RightsLink

Ultrastable Y zeolite (USY zeolite) is dealuminated Y zeolite, meaning there are fewer aluminium atoms in the framework.^[20] Less aluminium increases the Si/Al ratio, which consequently increases the hy-

drophobicity of the zeolite.^[21] Reasoning for why this is beneficial for CO₂ methanation is shown in section.2.3 Additionally, USY has a high thermal stability and contains mesopores (created by dealumination) and as micropores.^[15] The mesopores are beneficial as they provide more diffusion paths for reactants and products, as well as contribute to a higher external surface area.^[22] The micropores on the other hand are more shape selective.^[22] Overall, the combination of mesopores and micropores is beneficial for longer catalyst life and better performance which is why USY zeolites are appealing as catalysts.^[15;22]

2.3 Hydrophobicity

There exists a chemical equilibrium between the reactants and products in the CO₂ methanation reaction as shown in reaction equation 1.1.^[1] Removing water would shift the equilibrium to the right increasing the methane yield.^[2] Hence, for CO₂ methanation the zeolite should not have a strong affinity to water, and should provide pores that allow the water to exit.^[2] Studies have shown that USY zeolites, being quite hydrophobic are consequently well suited for CO₂ methanation.^[23]

2.4 Metals in zeolites

Metals incorporated into zeolites account for specific acid/base properties of the zeolite and ensure selective catalytic reduction of certain compounds.^[14] The basicity of the zeolite is strongly dependent on the polarizing effects of the cations added into the structure and the amount of cations.^[14;10] Larger cations have a lower electronegativity and consequently the zeolite's basicity is higher than for small cations.^[2] The number of cations is dependent on the number of aluminium atoms in the tetrahedral framework, since the aluminium provides the negative charges that attract cations.^[14]

A reason for adding metals into a zeolite is their potential to be reduced or oxidised.^[24] This property allows them to interact with components and activate them.^[24] Metal atoms available for reduction or oxidation are referred to as active sites.^[24] The amount of active sites is proportional to the catalytic performance.^[25] Consequently, the reducibility and ability to be oxidised of a metal in a zeolite is important for enhancing its catalytic properties.^[26] The reduction or oxidation of a metal depends on the reaction surroundings, the acidity, whether it has a strong interaction with the zeolite framework and temperature.^[26;27]

Metal dispersion corresponds to the fraction of metal atoms on the surface of a catalyst relative to the total amount of the metal atoms in the structure.^[28;29] The metal cations exposed to the surface are usually those that act as active sites, meaning a high metal dispersion is desirable for an increase in catalyst effectiveness.^[29] A high metal dispersion improves both the selectivity and the activation of reactant.^[2] The extent of metal dispersion is dependent on the method used to add the metal into the structure as well as the structure of the zeolite.^[2] Metal dispersion decreases through sintering which is observed in Ni based catalysts.^[2;8;9] In CO₂ methanation, the metal atoms interact with CO, which is often present as an intermediate in the CO₂ methanation reaction, and form metal carbonyls which result in metal sintering.^[7] Due to sintering, pores and active sites can be blocked and destabilization of the zeolite occurs.^[30] Research shows that sintering can be reduced through the addition of other cations, especially Mg and Ce show promising properties^[25;31;7].

2.4.1 Ion exchange and Impregnation

Metals are most commonly dispersed into the zeolites through ion exchange or impregnation.^[2] The dispersion method can have an effect on the catalytic activity.^[25] Adding metal cations through ion exchange is a process in which the protons or other cations which counterbalance the negative charges in the zeolite are exchanged by the added metal.^[21] In impregnation however a metal precursor is used to disperse the metal on the zeolite.^[21]

2.5 CO₂ methanation mechanism

The mechanism for the CO₂ methanation reaction (see equation 1.1) when using zeolites is under debate.^[3] The mechanism is apparently dependent on conditions such as the temperature, the type of compensating cations and the concentration of reactants.^[3] One assumes that CO₂ is either activated by forming complexes with metal ions or by forming carbonyls that interact with reduced Ni species (Ni⁰).^[3] Various studies agree that formate, HCOO⁻, is formed which adsorbs onto Ni⁰ enabling it to

react further to produce the CO intermediate.^[32;3] Therefore a reduction step is performed prior to CO₂ methanation.^[33]

3 Discussion

3.1 Ni/USY zeolites

Ni/USY zeolites are promising candidates as catalysts for CO₂ methanation.^[2] Here the dispersion method, in particular Ion exchange (IE) and Impregnation (IMP), the concentration of Ni and how the temperature influence the catalyst is analysed. The amount of Ni analysed is in the range of 4-15% and the temperature range considered is 350-450°C.

3.1.1 Effect of Ni dispersion method

The Ni dispersion method into the zeolite has consequences on the amount of active sites and hence the extent of CO₂ conversion (see section 2.4).^[7] The addition of 2%Ni through IE into USY changes the conversion from 3% to 4% (see (a) and (c) figure 3.1). This insignificant effect is because IE Ni leads to octahedrally coordinated Ni²⁺ which only reduce at higher temperatures (ca. 800°C) meaning it can not activate reactants or intermediates in the temperature range analysed (see section 2.5).^[7]

The addition of Ni through IMP leads to NiO and octahedrally coordinated Ni²⁺,^[7;34;25] NiO is more easily reduced than Ni²⁺, meaning it can interact with the reactants more effectively leading to an increase in the catalyst's effectiveness.^[7] IMP of 2%Ni has a strong effect on the USY catalyst effectiveness, increasing the conversion by 27% (see (a) and (d) in figure 3.1). Figure 3.1 also shows that 10%Ni/USY leads to 63% CO₂ conversion which noticeably exceeds the 5% conversion from 10%NiO + USY. This highlights that not only the reducibility of NiO is important but also the interaction between NiO and the USY zeolite which is more prominent in 10%Ni/USY.^[7]

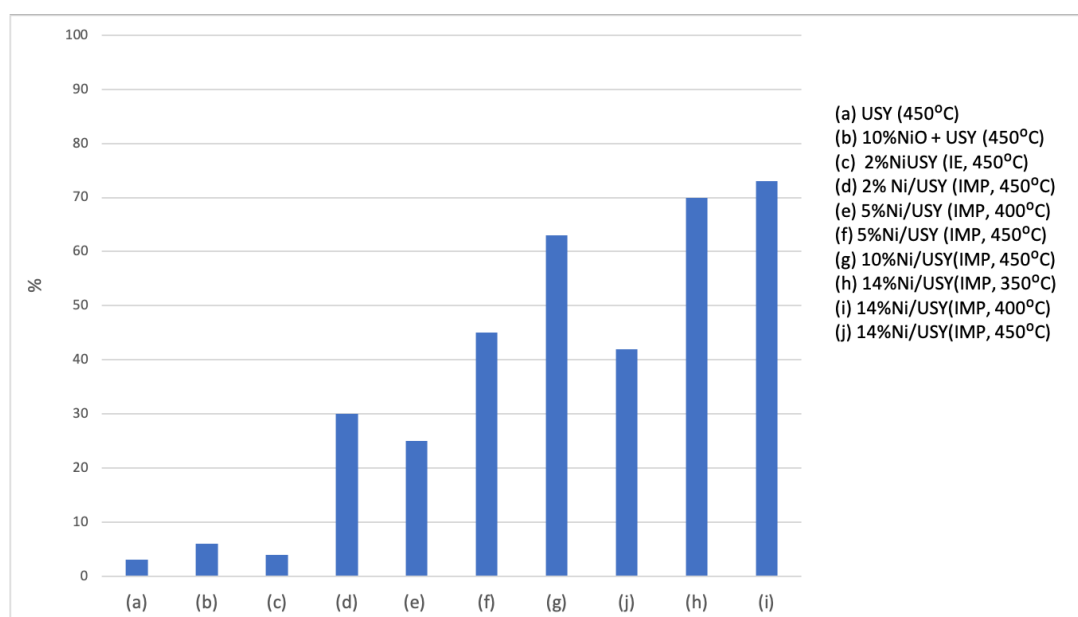


Figure 3.1: CO₂ conversion for Ni/USY zeolites with different Ni contents at 450°C. IE = Ion exchange and IMP = Impregnated. Results were acquired from reference Graca, I, et al.^[7] and Bacariza, M.C, et al.^[33].

3.1.2 Effect of Ni concentration

As shown in figure 3.1 by comparing (f) and (j), the conversion increases from 45% to 73% by increasing the Mg amount from 5% to 14%. This indicates that the more Ni is added through IMP the higher the CO₂ conversion. This is because a higher Ni content increases the NiO content, which can be reduced readily to provide more activation sites leading to a higher catalyst effectiveness.^[7] Data showing the effect of a higher Ni concentration dispersed through IE was not found.

3.1.3 Effect of Temperature

At 5%Ni/USY the conversion increased from 25% to 45% by increasing the temperature from 400 to 450°C (see figure 3.1). For 14%Ni/USY the conversion increased by 28% by increasing the temperature from 350 to 400°C. This indicates that the conversion increases with temperature. An explanation for these observations on 5%Ni/USY and 14%Ni/USY zeolites could be the Ni reduction dependence on temperature.^[35] NiO species are readily reduced at temperatures in the range of 350-420°C depending on their positioning in the zeolite.^[7] This would explain why at higher temperatures (ca. 450°C) there is a higher conversion as at this point there are more reduced Ni species able to activate reactants.

For zeolites with 5%Ni concentrations the influence of Ni on the CO₂ conversion is highest at 450°C (see (e) and (f) in figure 3.1).^[7;33] At 14% Ni concentration there is a high conversion (69%) even at 400°. Only at 350°C there is a smaller change in conversion (31%). One can conclude that lower concentrations of Ni are more dependent on higher temperatures than higher concentrations of Ni. This difference in temperature dependence can be due to the placement of the NiO species.^[7] More Ni leads to more NiO on the surface of the zeolite where they are reduced at lower temperatures (ca. 350°C) than when inside the zeolite structure.^[7] More reduced NiO species leads to more activation and could explain the difference in temperature dependence for high and low concentrations of Ni.

3.2 MgNi/USY

The effect Mg has on Ni/USY with respect to conversion of CO₂ methanation is evaluated here. For higher concentrations of Ni (ca. 15%) the effect Mg has on the catalyst with respect to temperature is taken into consideration. The temperature influence on low concentrations of Ni is not discussed here, as the effect is similar to the temperature effects observed for Ni/USY with no Mg dispersed in it (see section 3.1.3).^[7]

3.2.1 Influence of Mg in ca.5%Ni/USY

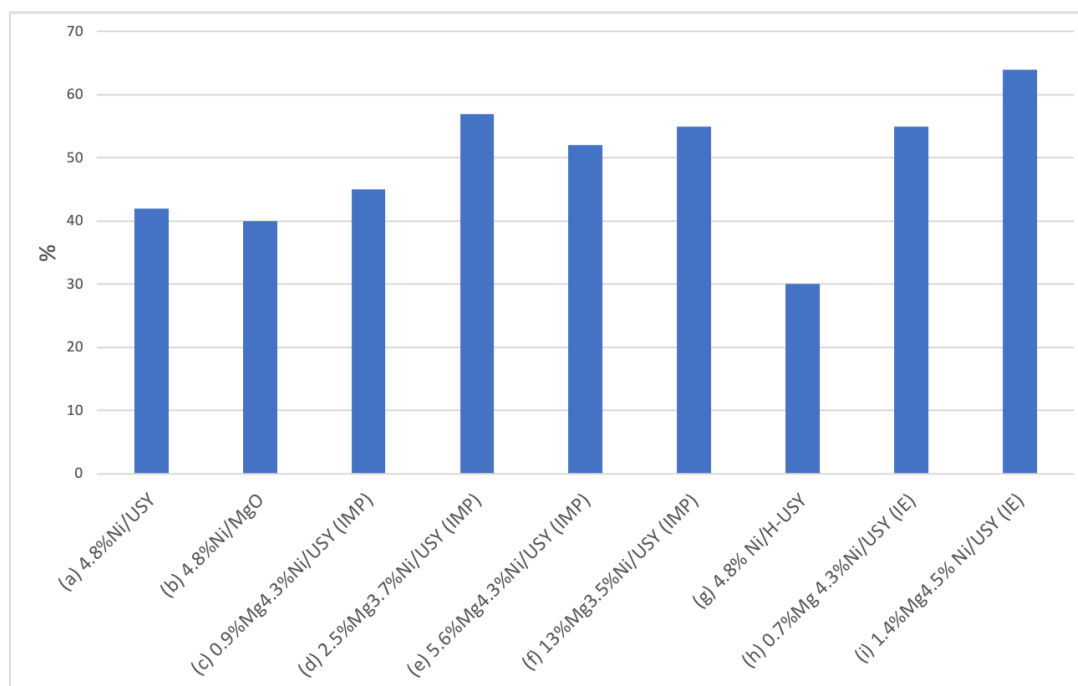


Figure 3.2: CO₂ conversion for Ni/USY zeolites with dispersed Mg at reaction temperatures at 450°C (IMP = Impregnation and IE = Ion exchange). For all the zeolites shown in the graph Ni was added through Impregnation. These results were acquired from Bacariza, M.C., et al.^[25].

The comparison of (a) and (d) in figure 3.2 shows a conversion increase from 42% to 57% by impregnating 2.5%Mg into USY. This indicates that Mg is beneficial for CO₂ conversion.^[25] This effect could be attributed to MgO which is formed as a result of IMP Mg.^[25] MgO enhances the activation of CO₂ as it binds to oxygen in CO₂ forming magnesium carbonate species.^[25;36;37] Additionally, it is hypothesized

that the interaction between Ni and MgO can prevent sintering, leading to an increase in catalyst effectiveness as strong bonds between reduced Ni and MgO stabilize Ni.^[38;25]

When 4.8%Ni/MgO was used as a catalyst for CO₂ methanation the conversion was less than for zeolites with IMP Mg (17% difference between (b) and (d) in figure 3.2). This indicates that the interaction between MgO and the zeolite is important. It is assumed that MgO interacts with reduced Ni or NiO but the exact way it interacts and influences the zeolite is unclear.^[25]

Zeolites (c) and (d) in figure 3.2 show that an increase from 0.9% to 2.5%Mg increases the conversion from 45% to 57% and zeolites (d) and (e) show that an increase from 2.5% to 5.6%Mg lowers the conversion from 57% to 52%. This suggests that there is an optimal amount of IMP Mg. This could be because MgO contributes to a decrease in CO₂ conversion at Mg concentrations above 2.5% as a result of the formation of solid solutions, such as Ni_xMg_{1-x}O₂ and MgAl₂O₄.^[25] The molecules block pores and destabilizes micropores in the zeolite leading to a decrease in conversion.^[25] Additionally, the strong bond between NiO and MgO, impedes the reduction of Ni leading to less active sites (Ni⁰).^[25]

Zeolites (g),(h) and (i) in figure 3.2 show that Ion exchanging 0.7% and 1.4% into Ni/H-USY increase the conversion by 25% and 34% respectively. This indicates that CO₂ conversion increases with increasing IE Mg.^[25] This trend might be because of the formed Mg²⁺ ion which acts as a compensating cation.^[25] Experiments indicate that Mg²⁺ increases the Ni dispersion on the surface leading to more active sites (see section 2.4).^[25] Additionally, Mg²⁺ forms complexes with CO₂ which activate it as shown in figure 2.2.^[3] Further research on higher IE Mg concentrations would be interesting to determine if this trend continues or if at one point the addition of Mg has no longer any effect. It could be that at higher Mg concentrations other molecules such as Ni_xMg_{1-x}O₂, which are also present after IE Mg increase in concentration and end up blocking pores as was the case when Mg was added through IMP.

Comparison of (c) and (h) which have similar Ni and Mg concentrations in figure 3.2 shows that IE Mg leads to a higher conversion (55%) than IMP Mg (45%). This makes IE a more preferable dispersion method which is surprising as for Ni IMP lead to higher conversion than IE (see section 3.1.1). This could be because of the different effects the compensating cations have as mentioned above and in section 3.1.1. It is unclear why Mg²⁺ can activate the CO₂ molecules through complex formation but for Ni²⁺ this complex formation does not have an impact. Further studies could look into this.

For IE Mg little research as been done on the influence Mg²⁺ has on the Ni sintering in Ni/USY. Experiments indicate that Mg²⁺ has no interaction with Ni²⁺ or NiO in the structure meaning Mg²⁺ might not help against sintering.^[25] Perhaps the sintering effect is still present but the impactful Mg²⁺ activation of CO₂ compensates for it.

3.2.2 Influence of Mg in ca.15%Ni/USY

In figure 3.3 (a) and (e) show that the impregnation of 9%Mg to 13%Ni/USY has a conversion of 52% which is noticeably higher than the 35% reached by 14%Ni/USY at around 340°C. At 450°C (c) and (g) show that 9%Mg13%Ni/USY differs in terms of conversion to 14%Ni/USY only by 3%. This indicates that IMP Mg has a stronger effect on conversion at lower temperatures (ca. 340°C) than higher temperatures (ca. 450°C). This might be because the metal dispersion decreases due to sintering at higher temperatures.^[39;33] Perhaps, at 350°C the the beneficial effects of produced MgO species most effectively counteracts the sintering effect (see effects of MgO in section 3.2.1). The MgNi/USY zeolite with IMP Mg analysed was 9%Mg13%Ni/USY, has a higher Mg and Ni content than those analysed for low Ni contents (see section 3.2.1) which would explain why this sintering effect was not observed for lower Ni concentration. 9%Mg13%Ni/USY was analysed because this was calculated to be the optimum amount of Mg for this Ni content before blocking of pores and structural damage occurs as described in section 3.2.1.^[25] However, sintering was not taken into account meaning 9%Mg13%Ni/USY might not have the optimum Mg concentration. It is peculiar though why MgO does not help against sintering as it did for lower Ni concentrations (see section 3.2.1). Perhaps, at higher Ni content there is too little MgO to stabilize Ni (see section 3.2.1).

Zeolites (h) and (k) in figure 3.3 show that IE 0.7%Mg to USY can change the conversion from 42% to 61% at around 400°C. However, at 450°C these zeolites (see (i) and (l) in figure 3.3) only differ by 8% change. Similar observations are made for IE 1.4% Mg (see (h),(n) and (o)). This indicates that the influence of IE Mg depends on the temperature. This is the same observation made for IMP Mg and can possibly also be explained through sintering.^[25]

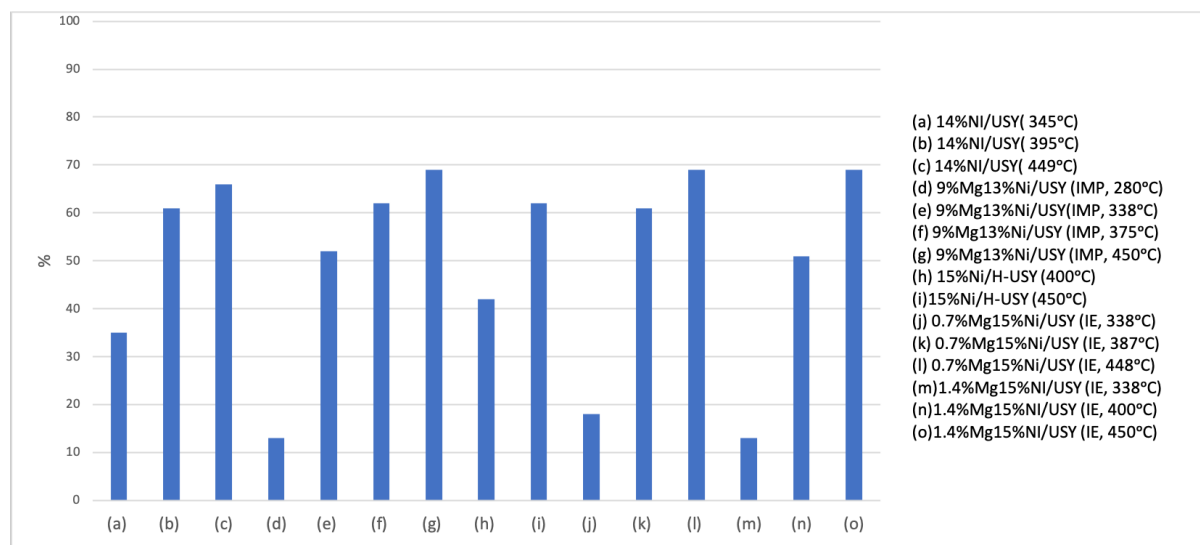


Figure 3.3: CO₂ conversion as a function of temperature for different MgNi/USY zeolites (IMP = Impregnation and IE = Ion exchange). For all the zeolites Ni was added through Impregnation. For 15%Ni/H-USY the USY zeolite was first treated with NH₄NO₃ and consequently impregnated with Ni^[25]. The results were acquired from two studies from Bacariza, M.C. et al.^[25:10].

Comparison of (k) and (n) in figure 3.3 shows that 0.7% IE Mg leads to a higher conversion (61%) than 1.4% IE Mg (51% conversion). It is theorized that this could be due to the formation of Ni and Mg oxides when too much Mg is present.^[25] These oxides can lead to a decrease the reducibility of Ni.^[25] However, it is odd that this effect is not observed for low concentrations of Ni. Further studies could look into this (see section 3.2.1).

In figure 3.3 (k) shows that IE 0.7%Mg leads to 61% conversion at 387°C and (f) shows that 9% IMP Mg leads to 62% at 375°C. Considering these conversions are similar one can conclude that IE Mg is better as less Mg is required compared to IMP Mg to reach the same conversion.

Two observations made in the figure 3.3 are due to Ni. First of all the conversion increased with temperature as shown in figure 3.2.2 for IMP and IE. This effect can be because of the increase in reduced Ni species as explained in section 3.1.3. Secondly, through comparing figures 3.2 and 3.3 one can see that the same amount of Mg at different Ni concentrations leads to higher conversion for higher Ni concentrations (comparison of (h) and (i) from figure 3.2 with (n) and (o) from figure 3.3). This difference in conversion can be attributed to the amount of Ni as discussed in section 3.1.2.

3.3 CeNi/USY

In zeolites with IMP Ce, CeO₂ forms which promotes CO₂ activation by providing activation sites for CO₂ on which reduction to CO can occur^[7:40]. This section focuses on zeolites with IMP Ce and IMP Ni. Research analysing IE Ce in Ni/USY for CO₂ methanation has apparently not been conducted.

3.3.1 Influence of Ce in ca. 5%Ni/USY

At about 5%Ni the addition of Ce increases the CO₂ conversion.^[7] Experiments show that around 350°C the influence of Ce is limited (only a 2-4% change in conversion) however at around 400°C the addition of Ce in Ni/USY has the strongest effect, with conversion changing by 35% with 15%Ce and 25% with 7%Ce compared to Ni/USY.^[7] At higher temperatures, Ce still increases the conversion but its effect decreases.^[7] The stronger increase in CO₂ conversion at 400°C might be related to the CeO₂ molecules. An experiment found that CeO₂ can increase the CO₂ adsorption in a catalyst strongly already at 300°C.^[40] Hence, Cerium's noticeable influence at 400°C in CeNi/USY might be due to CeO₂ dependence on temperature. However it is unclear whether the temperature influence is only due to CeO₂.^[40]

A higher Ce content leads to a higher CO₂ conversions as 15%Ce5%Ni/USY has a conversion of 62% but 7%Ce4%Ni/USY only reaches 55% at 450°C. This could be because more Ce leads to more CeO₂

molecules which increase the activation and with that the conversion.

3.3.2 Influence of Ce in ca. 15%Ni/USY

For a higher Ni content the Ce has a similar effect as for lower Ni concentrations in Ni/USY.^[7] The difference is that for higher Ni concentrations the conversion is higher with the same amount of Ce (7%Ce14%NiUSY and 7%Ce4%NiUSY reach conversions of 71% and 58% respectively at 450°C).^[7] This increase is expected considering the effect of a higher Ni content (see discussion in section 3.1).^[7] Research also shows that the interaction between Ni and CeO₂ is important for a satisfactory CO₂ conversion).^[7] This also explains why CeNi/USY zeolites with high Ni content have a higher conversion than those with lower Ni content as there are fewer Ni species to coordinate with.

One difference between 4%Ni and 14%Ni is the temperature at which Ce has the strongest influence. For 14%Ni, Ce has the largest influence in the range 320- 360°C with 7% Ce leading to a conversion increase of 24% relative to 14%NiUSY.^[7] Experiments indicate that this is because of CeO₂ and its dependence on temperature as explained in section 3.3.1. For lower Ni concentrations, 7%Ce has the biggest effect at 400°C. Considering that the CeNi/USY zeolites discussed here only differ in their Ni content (5% and 14%) the Ni must be the reason for the difference in temperature dependence. The temperature observations could be due to an increase in reduced Ni species as the temperature where Ce has the strongest influence is where NiO species are most readily reduced (see section 3.1.3). Compared to low Ni concentrations (4%), higher Ni concentrations (14%) have a larger amount of NiO species on the surface. These species are reduced at lower temperatures than in the structure (see section 3.1.3) and would explain the different temperature dependence of the zeolites.

The CeO₂ could also lead to a decrease in sintering in Ni/USY because of its interaction with Ni species as was the case for IMP Mg (see section 3.2). This hypothesis is supported by another experiment which found that the incorporation of Ni into a Ce oxide species lead to less sintering.^[41]

There are apparently no studies which investigate higher Ce contents (>7%) for Ni concentrations in the range of 14%. For lower Ni contents, the higher the Ce concentrations the higher the CO₂ conversion, as mentioned in section 3.3.1. Hence, further research where the concentration of Ce is increased might be an interesting research area to pursue to perhaps reach higher conversions at lower temperatures.

3.4 Comparison of Mg and Ce

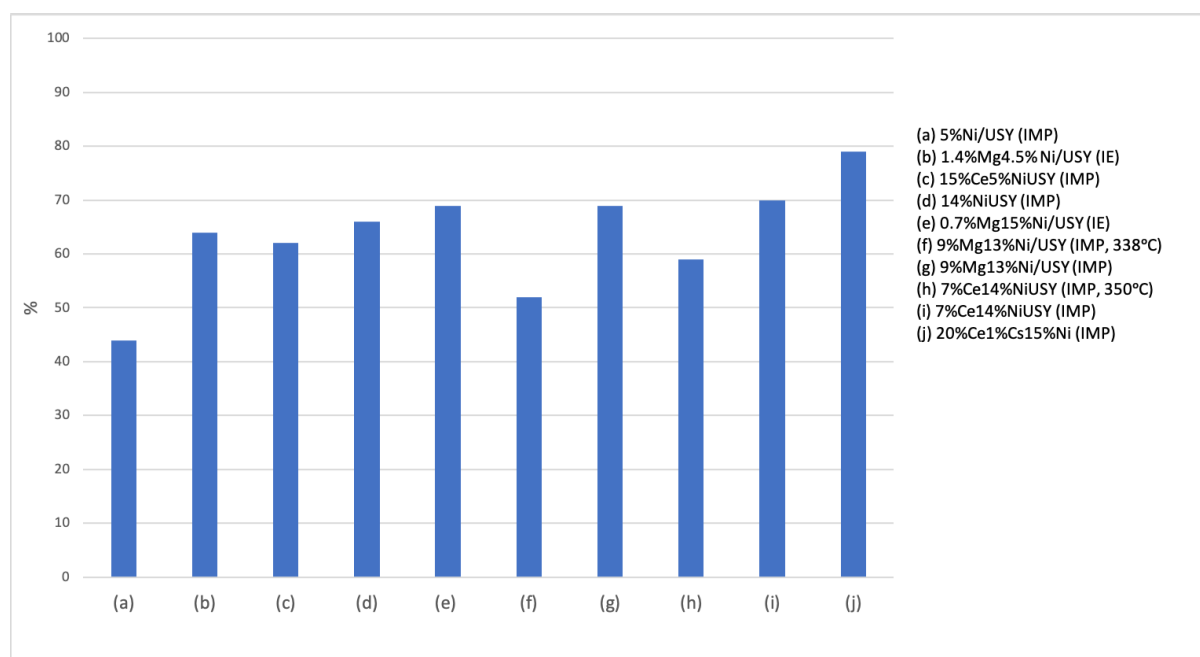


Figure 3.4: These are the CO₂ conversion values for Ni/USY zeolites with Mg,Ce and Cs dispersed. Unless otherwise indicated the data corresponds to processes run at 450°C. The data comes from Bacariza, M.C, et al.^[31;25] and Graca, I et al.^[7].

Figure 3.4 shows the CO₂ conversion of zeolites that were considered most suited amongst those discussed previously in this report. For low concentrations of Ni in MgNi/USY the 1.4%Mg4.5%Ni/USY catalyst appeared best compared to the other zeolites shown in figure 3.2 as it had the highest CO₂ conversion of 64%. For higher concentrations of Ni in MgNi/USY the apparently most suited catalyst amongst the zeolites presented in figure 3.3 is 0.7%Mg15%Ni/USY as it has a conversion of 69% at 450°C and requires little Mg content relative to the other zeolites discussed which reach similar conversions at those temperatures. For lower temperatures the 9%Mg13%Ni/USY is more beneficial as it leads to a CO₂ conversion above 50% below 340°C and reaches up to 69% at 450°C. No other catalyst in figure 3.3 reaches the same conversion at already 340°C. For CeNi/USY with low Ni concentrations the most suited catalyst is 15%Ce5%Ni/USY as it leads to the highest CO₂ conversion of 62%. However, it is likely that higher Ce contents might lead to a greater conversion. For higher Ni concentrations in CeNi/USY the best zeolite in terms of conversion from those analysed was 7%Ce14%Ni/USY with 80% conversion.

Figure 3.4 indicates that for low concentrations of Ni 1.4%Mg4.5%Ni/USY is the best catalyst. However, Ce in 15%Ce5%Ni/USY already influences the conversion noticeably at 400°C leading to 56% which could be an argument for using Ce. Additionally, the Ce5%Ni/USY might be better if more Ce is used as mentioned in section 3.3.1. However, in 1.4%Mg4.5%Ni/USY only a 1.4% Mg are required which is useful in terms of cost. Overall, it appears that 1.4%Mg4.5%Ni/USY is the most suited amongst those analysed if the reaction is run at higher temperatures.

For high concentrations of Ni the addition of Mg and Ce to Ni/USY is insignificant at 450% as the conversion changes at most 4% as shown by zeolites (d),(e),(g) and (i) in figure 3.4. Hence, if one wants to run the reaction at 450°C the addition of Mg and Ce is arguably unnecessary. However the beneficial effect of Mg and Ce is more noticeable at lower temperatures. At 338°C 9% IMP Mg can increase the conversion up to 62% and at 350°C 7% IMP Ce can lead to 59% conversion (see (f) and (h) in figure 3.4). Considering the slight difference in temperature for those values the difference in conversion reached by 9%Mg and 7%Ce is not that large and both appear equally effective. In general, they have a strong influence on the conversion as discussed in sections 3.2.2 and 3.3.2 and hence are useful in Ni/USY for catalysing CO₂ methanation at about 350°C.

Perhaps the combination of Mg and Ce in Ni/USY for CO₂ conversion is a research area one can pursue. Experiments have investigated the combination of Ce and Cs in Ni catalysts and found that it can increase the catalyst's effectiveness strongly.^[31] The 20%Ce1%Cs15%Ni/USY leads to CO₂ conversions of 75% at temperatures of already 270°C.^[31] The combination of metals appears to be beneficial especially the combination of Mg and Ce might be interesting as already on their own they are arguably useful

4 Conclusion

Conversion of CO₂ into methane is a promising method to reduce the CO₂ concentration in the atmosphere. Research indicates that Ni/USY zeolite is well suited to catalyse this reaction and that the catalyst effectiveness can be improved by the dispersion of metals such as Mg and Ce, which was the topic of this present report.^[2] The temperature range analysed was in the range of 280- 450°C.

It was found that the CO₂ conversion increased from 45% to 73% by increasing the Ni content from 5% to 14%. This was mainly explained by a higher NiO concentration. Furthermore, the conversion increased with temperature, which was attributed to a higher amount of reduced Ni. Zeolites with a lower Ni concentration (5%) showed a higher dependence on temperature than those with higher concentrations of Ni (14%). This effect was attributed to more NiO on the zeolite surface at higher Ni concentrations making it less dependent on temperature.

The dispersion method used for adding Ni and Mg into the zeolite had an effect on the CO₂ conversion. A comparison of dispersion method for Ce was not conducted due to lack of literature. For Ni, addition through IMP seemed the most beneficial whilst for Mg the dispersion through IE was found to be best due to the formation of Mg²⁺ which activated CO₂. IMP Mg lead to MgO species that helped activate CO₂ and prevented sintering however it was found that there was a limit to how much IMP Mg could be added before conversion decreased. Overall, the dependence on the dispersion method is linked to the chemical species produced by the addition method. However, the exact effect of the species is not yet fully understood.

In general one can conclude that for lower temperatures, a high Ni content (ca. 15%) and a high amount of IMP Mg (9%) or Ce (7%) is beneficial for conversion. Mg and Ce lead to similar conversion values. For higher temperatures, reasonable conversion can be reached with low Ni concentrations and the addition of IE Mg and IMP Ce. Where IMP Ce lead to CeO₂ which helped activate CO₂ and hence increase conversion. It was concluded that 1.4%Mg4.5%Ni/USY with IE Mg was the best suited catalyst as it led to the highest conversion and the metal amount required was little compared to others zeolites. For higher temperatures a higher Ni content can also be used for a high conversion however then the addition of Ce or Mg is arguably unnecessary as it improves conversion only by a few percent.

Further studies could look into the combination of Ce and Mg, and how CO₂ conversion is influenced by even higher contents of Mg and Ce added through Ion exchange and impregnation respectively.

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