Influence of Support on Ni Catalyst Performance in DRM

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Abstract- The present work examined the impact of various support materials on the type of Ni-based catalysts and their activity in the methane dry reforming reaction. The study's characterization methods include determining the surface area of the catalysts using the N2 physisorption technique, x-ray diffraction, and thermogravimetric analysis. As it was established from the research, the support material affected the NiO species in the catalyst. Supports material like CeO₂ displayed feeble binding with the NiO resulting in easy reduction of the catalytic during activation. Nonetheless, this weak interaction can also lead to quicker deactivation due to the aggregation of the active Ni species. On the other hand, ZrO₂ also reacted with NiO though the extent of their interaction was higher than that of CeO₂. This could help greatly impede the reduction process required for activation.

This could lead to the preparation of support material with desirable textural characteristics and acceptable interaction of Ni with the support. These two factors helped in the dissemination and settling of NiO species. Therefore, the Ni catalyst supported on ZrO_2 exhibited enhanced performance in methane dry reforming.

These findings highlight the importance of support selection as a crucial component in achieving extremely high DRM catalytic stability and efficiency. The study's conclusions are still useful for developing new, sophisticated catalyst systems that would produce syngas with increased stability and activity and no environmental harm because of their low greenhouse gas emissions.

Keywords- Dry Reforming, Catalyst Performance, Zirconia, Ceria, Support

I. INTRODUCTION

The potential for dry reforming methane using carbon dioxide (CO_2) is presently regarded as one of the most significant viewpoints. This process offers a two-fold benefit: it does this by efficiently harnessing greenhouse gases (Methane; CO₂) and subsequently synthesizes useful synthesis gas (Syngas – a mixture of Hydrogen and CO) that can be used in Fischer-Tropsch (FT) reactions to produce fuels. Also, it depicts an opportunity that could transform renewable energy sources into chemicals [1-5].

The concurrent occurrence of the reverse water gas shift (RWGS) reaction (1) affects the synthesis of syn-gas from the dry reforming of methane, resulting in a syn-gas ratio below unity.

$CO_2 + H_2 \rightarrow CO + H_2$	(1)
$CH_{\ell} \rightarrow 2H_{2} + C$	(2)

$$CH_4 \rightarrow 2H_2 + C \tag{2}$$

$$2CO \rightarrow CO_2 + C \tag{3}$$

Despite its advantages for the environment, dry reforming methane has problems with carbon deposition brought on by methane breakdown (2) and CO disproportionation or the Boudouard reaction (3).

Besides, it offers a possible approach to utilize renewable electricity for creating chemicals. Though noble metals like Ru, Rh, Pt, Pd, and Ir are the most favored due to their high activity, selectivity, stability, and low coke production, the DRM reaction can also be carried out by a metal catalyst. However, due to less available and higher costs; thus, they have not found significant commercial use [6-8].

Ni-based catalysts are the most preferred option in this case. Due to their superior economic characteristics and equally satisfactory efficiency, they are considered to be more suitable to methane dry reforming.

However, DRM catalysts based on Ni have some drawbacks regarding their use in industry despite the noted economic benefits. In reaction conditions, the nickel particles can be sintered and thus /from/ to larger clusters of particles. This together with coke formation, can cause rapid deactivation of the catalyst. Thus, the development of efficient and stable Ni-based catalysts is significant for the application of DRM processes [9].

Researchers [10] acknowledged that has brought attention to the above-stated challenges include the following Strategies that have been proposed by researchers to tackle these challenges include the following. One of the focuses includes altering the nature of the support in the catalyst. This can be accomplished by choosing other support media, using certain preparation techniques, or applying activity adjusters.

A reaction system's catalyst support materials play a critical role in influencing the catalyst's stability and activity. These features include surface area, pore structure, redox properties, and metal-support interactions that impact performance. large surface area Strong metal-support interactions increase the catalyst's stability and prevent sintering, whereas supports can greatly improve metal dispersion.

Carbon deposition may also be controlled by choosing the right support material. It has been claimed that promoting supports with lower Lewis acidity and/or basicity, including MgO and ZrO₂, provides higher resistance. Strong metal-support interactions and the supports' excellent thermal stability help to limit Ni nanoparticle sintering and maintain high catalytic activity over the course of the service life [11-14].

MgO, Al₂O₃, ZrO₂, CeO₂, and La₂O₃ are among the ceramic oxides that have been employed as Ni catalyst supports [11, 15-16]. It has been demonstrated that the coke deposition rate in DRM is inhibited by supports with reduced Lewis's acidity and/or basic site, such as MgO, ZrO₂, and La₂O₃[17-19].

On the other hand, some of the supports such as CeO₂ and ZrO₂ are known to have high oxygen storage capacities. Ni catalysts, act as supports or promoters to improve nickel dispersion; this is an important factor in maintaining resistance against particle sintering. The literature has already documented oxygen vacancies in CeO₂ and ZrO₂based catalysts. Ion vacancies facilitate charge transfer, intermediate oxidation, and reactant adsorption and activation. A CeO2 and ZrO2 material with a high capacity for storing oxygen may readily fill new oxygen vacancies and transfer oxygen with the gas phase. Indeed, the catalytic oxidation of carbon dioxide and methane during the DRM process depends on these mobile oxygen vacancies [20-23]. Besides these conventional supports, mesoporous (ZrO₂) molecular sieves are emergent due to highly developed specific surface area, neutrality, and thermostability which are profoundly required for DRM catalysts.

It is, however, well established that the physicochemical characteristics of a catalyst can be affected by the structural type of support material used. Even though prior work [24] has established that a wide variety of methods of preparing Ni-based zirconia and ceria catalysts results in the production catalysts with unique properties, of few comprehensive comparative studies aimed at understanding the synergistic influence of the morphology and structure of zirconia and ceria support the features of the catalyst and its efficiency in DRM. Therefore, there is a need for the present study to offer a synthesis of these relationships, which is lacking in the existing literature. Intensive and coke resistant catalysts are desirable for MDR hence the need to design highly active and coke resistant catalysts. This paper undoubtedly proves that the choice of an appropriate support material can improve the performance of the catalysts. Thus, the goal of this paper is to investigate the impact of various supports on Ni-based catalysts in the process of DRM of methane with CO₂.

To address the questions raised regarding the impact of the support material on the catalyst's performance, this study investigated the metal's interaction with the supports as well as the dispersion and distribution of NiO species on various supports. It would finally help in choosing proper supports for the construction of applicable Ni-based catalysts in industrial scale uses.

II. CATALYST PREPARATION VIA WET IMPREGNATION

The wet impregnation approach was used to synthesize the Ni-based catalysts. In this approach, an accurately calculated volume of the selected support material was dissolved in a solution of the nickel complexing agent (nickel nitrate in this case). The obtained mixture was further left for some other time, which depends on the type of process, to enable the adsorption of the precursors to the support. After the aging step, the solid was collected by drying, and then the sample of the catalyst was calcined at 600°C to form the active phase of the catalyst completely. This method enabled the achievement of uniform nickel loading on all the prepared catalysts. The prepared catalysts are labeled as NIZ-100 for Ni/ZrO2 and NIS-100 for Ni/CeO₂.

2.1 Catalyst Characterization

The N₂ adsorption-desorption isotherm at 77 K from the Nova 2200e Quanta chrome adsorption analyzer was used to calculate the BET surface area, pore volume, and average pore diameter of the catalyst samples. This technique is quite useful because it reveals information concerning the extent of the solid mass' pore size and reactant access space within the catalysts. To identify the phases included in the calcined catalysts, an XRD analysis was conducted using a Bruker D8 Advance X-Ray Diffractometer. This information helps to understand the chemical makeup and crystalline structure of the active ingredients and fillers.

Lastly, samples of spent catalyst were analyzed using thermogravimetric analysis (TGA) to assess the thermal stability of the samples. In this experiment, the samples were heated in air at a rate of 10K/min to a temperature between 293 K and 1073 K. These weight changes may also indicate the presence as well as the decomposition behavior of any residual materials and/or coke deposits on the catalysts.

2.2 Catalyst Performance

The catalytic performance of the NIS-100 and NIZ-100 catalysts for DRM were investigated in a fixedbed flow reactor system. To the reactor, a sample of the catalyst was added. Conducting a reduction pretreatment was the first process that the catalyst went through before the reaction could start. The catalyst was exposed to an H₂/N₂ gas mixture at 700°C for one hour in order to activate it and initiate the reaction. The catalyst's nickel oxide (NiO) is reduced to metallic nickel in this step. Following the reduction phase, the reactor's temperature was raised to 750°C. The reactant gas mixture which had methane and carbon dioxide at an equimolar stoichiometric ratio was then fed into the reactor. The components of the reactant and product gases were examined using a gas chromatograph fitted with a thermal conductivity detector. The following formulas were used to compute the conversions of carbon dioxide and methane.

$X_{CH4}(\%) = 100 \times F_{CH4in} - F_{CH4out}/F_{CH4in}$	(1)
$X_{CO2}(\%) = 100 \times F_{CO2in} - F_{CO2out}/F_{CO2in}$	(2)

III. RESULTS AND DISCUSSIONS

3.1 BET

H₂ chemisorption data are given in Table 1; the metal dispersion was estimated by the extent of metal particle scattering on the support. The outcome was fairly clear that the type of support material serves much influence in the dispersion of the metal. Additionally, the results showed that NiO/ZrO₂ had the maximum metal dispersion among all the catalysts. This could be explained by the support material's higher surface area, zirconia, which appears to promote the accommodation of Ni particles the catalyst prepared, namely NIS-100, the metal dispersions were relatively low. That is because support materials have a lesser surface area than zrO2 and a lesser surface area means a lesser number of active sites for the adsorbent to adhere to. Analyzing the obtained data, it is possible to observe that impregnation leads to the reduction of the specific surface area and total pore volume. The main reason for this result is because the nickel species partially obstructs the ceria support's pores in which it is deposit, so that they cannot in a meaningful way be penetrated by N₂ molecules during the physisorption of the last analysis [25].

Figures 1 and 2 show the nickel catalysts' nitrogen adsorption-desorption isotherms and pore size distribution, respectively. From the pore size distribution graphs, it can be observed that the overall shape of the curve is rather maintained. With the help of the H_2 chemisorption results, Table 1 also displays the average metal grain size and the typical surface area measurement for each catalyst.

It was reasonable to anticipate that metal dispersion increases with an increase in the specific surface area of active metal, which in turn confirmed that higher dispersions correspond to the larger active metal surface area.

Conversely, the metal dispersion was shown to be inversely related to the metal particle size. NiZ-100 had the smallest metal particle size and the largest active metal surface area of all the catalysts that were made. Such results corroborate with the research done by Keiichi [26] and Xu.[27] highlighting increased metal dispersion augments activity of the catalyst as well as its immune system to carbon formation. This implies that NIZ-100 which has the highest dispersion may also show the best results in the dry reforming reaction.



Figure 1: N₂ Adsorption Isotherms

Table 1: Textural Properties of Catalyst				
Catalyst	Surface Area (sg) m ² /g	Pore Volume (cm ³ /g)	Particle Size (cm ³ /g)	
Ni/CeO ₂ (NIS-100)	42.3	0.12	17.6	
Ni/ZrO ₂ (NIZ-100)	50.2	0.18	23.1	



Figure 2: Pore Size Distribution of the Catalysts

3.2 XRD

These peaks are also labeled in the XRD pattern of NiO/CeO₂ as depicted in Figure 3 where the broad peak at about 22° indicates that the ceria support is amorphous. Further, they found sharp peaks in the range of (JCPDS card no. 47-1049) at 37. 3°, 43. 3°, and 62. 8°, for NiO, belongs to the (111), (200), and (220) crystal planes. This further substantiates the fact that well-crystalline NiO species are anchored on the ceria support. This is because CeO₂ has a

smaller surface area than other support materials. The weak contact between NiO and the support, which may enhance the mobility and aggregation of NiO species during the high-temperature calcination, may be the cause of the prominent NiO peaks in the XRD pattern [28].

The catalytic performance of the NIS-100 and NIZ-100 catalysts for DRM were investigated in a fixedbed flow reactor system. To the reactor, a sample of the catalyst was added. Conducting a reduction pretreatment was the first process that the catalyst went through before the reaction could start. The catalyst was exposed to an H_2/N_2 gas mixture at 700°C for one hour in order to activate it and initiate the reaction. The catalyst's nickel oxide (NiO) is reduced to metallic nickel in this step. Following the reduction phase, the reactor's temperature was raised to 750°C. The reactant gas mixture which had methane and carbon dioxide at an equimolar stoichiometric ratio was then fed into the reactor.



Figure 3: XRD Analysis of the Catalysts

3.3 Influence of Support Material on Catalytic Performance

Consequently, materials used as support have been reported to have a profound influence on the nickelbased catalyst during methane dry reforming reactions as presented in Figure 4. The NiZ-100 shows highest conversions in the terms of methane and carbon dioxide conversions as (45% & 49%) respectively. This can be considered depending on several factors: the dispersion of the metal, the strength of the interaction between the metal and the support, and the characteristics of the support material [29].

NiS-100 catalyst has a high initial activity level. However, this activity gradually diminishes which shows that the company has poor stability. This situation can be attributed to the fact that the interaction between NiO and CeO₂ phases is relatively poor and also has less surface area [30]. This weak interaction does not effectively hinder the sintering, or agglomeration of the active nickel metal species on the surface of the ceria during the reaction. The advisability of employing the Ni/ZrO₂ catalyst created in this work as more effective is also addressed by these findings. There are multiple reasons for the increased catalytic activity, including: Ni's advantageous interaction with ZrO₂ support in particular may improve metal dispersion and inhibit sintering, which would improve catalyst stability. The specific preparation method employed in this investigation may result in a novel catalyst microstructure and greater active site availability. High catalytic activity may be explained by the synergistic combination of an ideal Ni particle size, a high surface area, and efficient metal-support interactions.



Figure 4: Performance evaluation of the catalysts in the terms of CH₄ Conversion (%) and CO₂ Conversion (%)

Because of the catalyst's lower reduction temperature and relatively extensive metal dispersion, zirconia (ZrO₂) is a commonly used support material for methane dry reforming. These elements most likely play a part in NiZ-100's superior methane dry reforming performance. At reaction conditions of 750°C and a high gas hourly space velocity (GHSV) of 70,000 mL/(gcat·h). With a negligible drop in conversion after 90 minutes on stream, it also exhibits exceptional stability, indicating strong catalytic activity and coking resistance, the NiO/ZrO2 catalyst achieves near-equilibrium conversions of both CO₂ and methane 41% %34%) respectively as shown in Fig 5. Additionally, it demonstrates remarkable stability, with a minimal decrease in conversion after

90 minutes on stream, suggesting high catalytic activity and resistance to coking.

Methane conversion in the provided study is higher than in numerous other works, according to a comparison of the results obtained in this work with data from the literature. For instance Dekar et al. [31] reported that using Ni/La₂O₃ catalysts alone at a reaction temperature of 800^oC resulted in a 20% methane conversion. As a result, another study likewise found that the DRM reaction for Ni-ZrO₂ produced a 23% methane conversion at 700°C [32]. Other literature has also demonstrated that similar reaction conditions result in decreased methane conversion [33-36].

Due to the low interaction between ZrO_2 and NiO, it was found that the NiO/ZrO₂ catalyst of this study possesses low stability in a severe reaction environment. Even if the low activity of the weak interaction may explain the high initial activity, it may also trigger sintering and nickel particles' agglomeration during the high-temperature reaction phases, which leads to fast deactivation in the long run [37].



Figure 5: Stability of the catalysts in the terms of CH₄ Conversion (%) and CO₂ Conversion (%)

3.4 TGA

Fig. 6 shows the thermogravimetric analysis of the TGA data of the catalysts that were used. The desorption of water molecules adsorbed on the catalyst's outer and interior surfaces has been attributed to the weight loss observed in the 500 K and below range.

The weight of all catalysts rises over 500 K, reaches its maximum at about 700 K, and then slightly falls

as the temperature rises to 1030 K. The oxidation of metallic nickel to NiO may be the cause of the first weight rise [38]. The latter weight loss can then be attributed to oxidation of the deposited carbon species on the surface.

The problem of carbon deposition during methane dry reforming is quite famous and is a source of catalyst deactivation. Thus, two main processes, methane dissociation and the Boudouard reaction, are thought to cause carbon formation on the catalysts [30]. Carbon deposition is a well-known issue causing catalyst deactivation during methane dry reforming. It's believed that methane dissociation and the Boudouard reaction are the primary mechanisms leading to carbon deposition on the catalysts [30].

The amount of carbon deposited on each catalyst during the process was measured using thermogravimetric analysis (TGA). The results indicate a significant variation in coking propensity among the catalysts. NIS-100 exhibits the highest weight loss (84%), suggesting severe carbon deposition. NIZ-100 shows lower weight losses 76%. Interestingly, NIZ-100 catalyst exhibits lower weight loss, suggesting minimal carbon deposition after the reaction.



Figure 6: Thermogravimetric Analysis of the catalysts

IV. CONCLUSION

This work investigated how nickel (Ni)-based catalysts for CO₂-mediated methane dry reforming processes were affected by various support materials, such as zirconia (ZrO₂) and cerium oxide (Ceria). Understanding how the support material affects the status of NiO species in the catalyst and, consequently, the catalyst's performance was the aim of the study. Thus, the outcomes of the study showed that there is a positive interlink between the support material and both the reduction characteristics and the Ni catalysts' efficiency. It can, therefore, be stated that supports like CeO₂, had weak interaction with NiO. This weak interaction allowed the reduction process during catalyst activation to reduce the standards. However, this benefit came with a potential drawback: The weak interaction

might also go a long way in contributing to faster deactivation because of agglomeration and clumping of the active nickel species.

On the other hand, it was found that Ni/ZrO₂ exhibited a more suitable behavior of these contradictory behaviors. The process leads to the development of a support material with required textural characteristics and quite a good interaction with the deposited nickel metal and the support. The dispersion and stabilization of NiO species on the support were facilitated by this alignment. Thus, in methane dry reforming, the Ni catalyst supported on zirconia shown outstanding activity, particularly when the gas's GHSV reached 70000 h-1. Nonetheless, it demonstrated exceptional steadiness throughout a 90-minute endurance test. Zirconia is a type of high-performance support material for Nibased catalysts utilized in methane dry reforming reactions, according to these findings.

These findings demonstrate the importance of support materials in determining the catalytic activity of Ni-based catalysts for DRM. Explain how the catalytic performance is affected by additional modifications to the support system, such as doping with different metal oxides or the creation of mixed oxide supports. To achieve improved metal dispersion and to define and regulate the catalyst's morphology, the preparation methods for catalyst creation, such as co-precipitation, sol-gel, and atomic layer deposition, should be precisely calibrated. To improve knowledge of the pathways of deactivation and the mechanisms of the reactions, investigations should be supplemented with the following techniques: DRIFTS, XAFS, and in-situ The structure and advancement of the Ni-based catalyst for DRM are primarily understood thanks to this work. By carrying out further research in these areas, we can enhance the catalytic processes for syngas generation and move closer to the future energy sector while using less nonrecurring resources.

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