

**ACTIVE FIBROUS STRUCTURED SILICA METAL OXIDE-  
SUPPORTED NICKEL CATALYSTS FOR DRY REFORMING OF  
METHANE**

BY  
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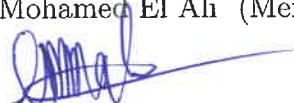
DEANSHIP OF GRADUATE STUDIES

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*To my family, whose unwavering support has shaped me into the person I am today, I owe everything. Their encouragement and guidance have been the driving force behind my perseverance and dedication in my life.*

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# LIST OF ABBREVIATIONS

|                      |                                                    |
|----------------------|----------------------------------------------------|
| ATR                  | Auto-thermal reforming                             |
| BE                   | Binding energy                                     |
| BET                  | Brunauer–Emmett–Teller                             |
| BJH                  | Barrett–Joyner–Halenda                             |
| BSE                  | Backscattered electron                             |
| CNTs                 | Carbon nanotubes                                   |
| CO <sub>2</sub> -TPD | CO <sub>2</sub> -temperature programmed desorption |
| DRM                  | Dry reforming of methane                           |
| EDX                  | Energy-Dispersive X-Ray                            |
| EELS                 | Electron energy loss spectroscopy                  |
| FESEM                | Field Emission Scanning Electron Microscopy        |
| FTIR                 | Fourier transformation infrared                    |
| FTS                  | Fischer–Tropsch synthesis                          |
| GHGs                 | Greenhouse gases                                   |
| H <sub>2</sub> -TPR  | H <sub>2</sub> -temperature-programmed reduction   |
| HSA                  | High specific surface area                         |

|                      |                                                    |
|----------------------|----------------------------------------------------|
| HT                   | Hydrothermal method                                |
| MSI                  | Metal-support interaction                          |
| NG                   | Natural gas                                        |
| NH <sub>3</sub> -TPD | NH <sub>3</sub> -temperature programmed desorption |
| NPs                  | Nanoparticles                                      |
| O <sub>Vs</sub>      | Oxygen vacancies                                   |
| OSC                  | Oxygen storage capacity                            |
| POM                  | Partial oxidation of methane                       |
| PT                   | Precipitation method                               |
| RWGS                 | Reverse water gas shift                            |
| SE                   | Secondary electron                                 |
| SEM                  | Scanning electron microscopy                       |
| SG                   | Sol-gel method                                     |
| SMSI                 | Strong metal-supporting interaction                |
| SPM                  | Scanning probe microscopy                          |
| SRM                  | Steam reforming of methane                         |
| TCD                  | Thermal conductivity detector                      |
| TD                   | Thermal decomposition method                       |
| TEM                  | Transmission electron microscopy                   |
| TGA                  | Thermogravimetric analysis                         |
| TOS                  | Time-on-stream                                     |

|     |                                   |
|-----|-----------------------------------|
| TPO | Temperature programmed oxidation  |
| WMO | World Meteorological Organization |
| XAS | X-ray absorption spectroscopy     |
| XPS | X-ray photoelectron spectroscopy  |
| XRD | X-ray diffraction                 |

# THESIS ABSTRACT

**NAME:** Mohammed Mosaad Awad

**TITLE OF STUDY:** Active Fibrous Structured Silica Metal Oxide-Supported Nickel Catalysts for Dry Reforming of Methane

**MAJOR FIELD:** Chemistry

**DATE OF DEGREE:** May 2024

*The dry reforming of methane (DRM) reaction has attracted significant attention due to its potential to mitigate carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) emissions while yielding valuable syngas. However, there remains a gap in understanding the synergistic interactions between catalytic activity and physicochemical features. This study addresses this gap by presenting a synthesis and performance evaluation of active fibrous-structured silica metal oxides-supported nickel catalysts for DRM, with the aim of achieving efficient syngas production. Two supports were developed and investigated for supporting the nickel active metal during the DRM reaction, each offering distinct advantages in catalytic activity and stability. The NSZF-10 catalyst incorporates zinc oxide as a co-support within the silica fibrous framework and is loaded with 10 wt.% nickel, resulting in enhanced hydrogen selectivity without com-*

promising catalytic performance. NSZF-10 demonstrated remarkable efficiency in the DRM reaction, achieving  $\text{CH}_4$  and  $\text{CO}_2$  conversions of 82% and 74%, respectively, over a 40-hour reaction period at 750 °C. Additionally, the NSZF-15 catalyst exhibited high  $\text{CH}_4$  and  $\text{CO}_2$  conversions of 87% and 88.7%, respectively, albeit with a slight decrease in  $\text{CO}_2$  conversion over time. The improved performance of NSZF-15 can be attributed to optimized textural and morphological properties, along with a strong metal-support interaction facilitated by zinc oxide. Two supports were developed and investigated for supporting the nickel active metal during the DRM reaction, each offering distinct advantages in catalytic activity and stability. Moreover, NSLF-10, a fibrous silica-lanthana-supported nickel catalyst, exhibited uniformly dispersed nickel, a strong metal-support interaction, and small nickel particle size. This catalyst achieved high conversions of  $\text{CH}_4$  and  $\text{CO}_2$  at 87% and 86.7%, respectively, with an elevated  $\text{H}_2/\text{CO}$  ratio. These findings highlight the potential of using fibrous-structured silica metal oxide-supported nickel catalysts for efficient syngas production through the DRM, paving the way for industrial-scale applications in the future.

## ملخص الرسالة

الاسم: محمد مسعد عوض

عنوان الدراسة: محفزات النيكل المدعمة بأكسيد المعادن النشطة ذات البنية الأليافية المصنعة من السيليكا لعملية الإصلاح الجاف

للميثان

التخصص: كيمياء

تاريخ الدرجة العلمية: مايو 2024

لقد اجتذب تفاعل الإصلاح الجاف للميثان (DRM) اهتمامًا كبيرًا نظرًا لقدرته على تخفيف انبعاثات ثاني أكسيد الكربون والميثان مع إنتاج غاز اصطناعي قيم. ومع ذلك، لا تزال هناك فجوة في فهم التفاعلات التآزيرية بين النشاط الحفاز والخصائص الفيزيائية والكيميائية. تتناول هذه الدراسة هذه الفجوة من خلال تقديم تقييم توليف وأداء لمحفزات النيكل النشطة المدعمة بأكاسيد فلز السيليكا ذات البنية الليفية لإصلاح الجاف للميثان، بهدف تحقيق إنتاج فعال للغاز الاصطناعي. تم تطوير ودراسة دعامتين لدعم معدن النيكل النشط أثناء تفاعل DRM، ويقدم كل منهما مزايا مميزة في النشاط التحفيزي والاستقرار. يشتمل المحفز NSZF-10 على أكسيد الزنك كدعم مشترك داخل إطار ليفي السيليكا ويتم تحميله بنسبة 10% بالوزن من النيكل، مما يؤدي إلى تحسين انتقائية الهيدروجين دون المساس بالأداء الحفزي. أظهر NSZF-10 كفاءة ملحوظة في تفاعل DRM حيث حقق تحويلات ثاني أكسيد الكربون والميثان بنسبة 82% و74%، على التوالي، خلال فترة تفاعل مدتها 40 ساعة عند 750 درجة مئوية. بالإضافة إلى ذلك، أظهر المحفز NSZF-15 تحويلات عالية من ثاني أكسيد الكربون والميثان تبلغ 87% و88.7% على التوالي، وإن كان ذلك مع انخفاض طفيف في تحويل ثاني أكسيد الكربون بمرور الوقت. يمكن أن يعزى الأداء المحسن لـ NSZF-15 إلى الخصائص التركيبية والمورفولوجية المحسنة، إلى جانب تفاعل قوي للدعم المعدني يسهل أكسيد الزنك. تم تطوير ودراسة دعامتين لدعم معدن النيكل النشط أثناء تفاعل DRM، كل منهما يقدم دعمًا متميزًا مزايا في النشاط التحفيزي والاستقرار. علاوة على ذلك، أظهر NSLF-10 وهو محفز نيكل ليفي مدعوم من السيليكا واللاتان،

نيكلًا مشتتًا بشكل موحد، وتفاعلاً قوياً مع الدعم المعدني، وحجم جسيمات النيكل صغيراً. حقق هذا المحفز تحويلات عالية بقيمة ثاني أكسيد الكربون والميثان عند 87% و86.7%، على التوالي، مع نسبة مرتفعة من الهيدروجين : اول اكسيد الكربون. تسلط هذه النتائج الضوء على إمكانية استخدام محفزات النيكل ذات البنية الليفية والمدعومة بأكسيد النيكل لإنتاج الغاز الاصطناعي بكفاءة من خلال لإصلاح الجاف للميثان، مما يمهد الطريق للتطبيقات على نطاق صناعي في المستقبل.

# CHAPTER 1

## INTRODUCTION

In the twenty-first century, energy has become crucial for sustaining economic growth and industrial production [5][6] with fossil fuels meeting over 90% of the world's energy demand[7]. However, the extensive exploration and consumption of natural fossil fuels over past centuries have led to their inevitable depletion. The combustion of these fuels, including coal, natural gas, oil, as well as solid waste, trees, and other organic matter, has released Greenhouse gases (GHGs) such as carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) into the atmosphere [7].  $\text{CO}_2$  and  $\text{CH}_4$  are the main contributors to GHG emissions, accounting for approximately 81% and 16%, respectively, and are widely recognized as the primary drivers of current climate change [8][9]. According to the World Meteorological Organization (WMO), the concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  in 2011 were assessed to be 1.813 and 390.5 ppm, respectively [10]. While  $\text{CO}_2$  has long-term effects,  $\text{CH}_4$  drives warming in the short term, with over 80 times the warming potential of  $\text{CO}_2$  during the first two decades after its release into the atmosphere [11][12]. Both natural sources and human activities contribute to  $\text{CH}_4$  production, with landfills alone contributing about one-third of  $\text{CH}_4$  emissions in the US [13][14].

CH<sub>4</sub> emissions originate from natural processes like termites, grasslands, coal beds, lakes, wetlands, and wildfires, as well as human activities such as landfills, oil and gas processing, wastewater treatment plants, coal mining, rice production, cattle ranching, and various agricultural practices [13][14]. In 2010, the total anthropogenic CH<sub>4</sub> emissions from all sources were estimated to be 6875 million metric tons of CO<sub>2</sub> equivalent [15]. CH<sub>4</sub> serves as the primary component of Natural gas (NG), accompanied by small quantities of other hydrocarbons like propane (C<sub>3</sub>H<sub>8</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and butane (C<sub>4</sub>H<sub>10</sub>). NG also contains inert diluents, namely molecular nitrogen (N<sub>2</sub>) and CO<sub>2</sub> [16]. NG reservoirs are often situated far from industrial complexes, sometimes offshore. Transporting NG to potential markets via pipelines may not be feasible, necessitating expensive liquefaction for shipment by ocean vessels, thus limiting its utilization [17]. Consequently, wasted hydrocarbons contribute significantly to global warming. This has spurred research on utilizing GHGs (CO<sub>2</sub> and CH<sub>4</sub>) to produce syngas (H<sub>2</sub>/CO), a topic of significant interest. Beyond serving as raw materials, they could offer a cleaner alternative to fossil fuels [18]. Additionally, syngas exhibits application in numerous industrial domains, such as methanol, chemical, and ammonia production, as well as the Fischer–Tropsch synthesis (FTS) as mentioned in Figure 1.1 [18][19].

Researchers have explored various techniques to produce syngas by reducing environmental CO<sub>2</sub> and CH<sub>4</sub> concentrations, utilizing them as feedstock for valuable chemical production. Among these techniques, Steam reforming of methane (SRM), DRM, Partial oxidation of methane (POM), and Auto-thermal reforming (ATR) have been identified as particularly effective for syngas production, with SRM being the

predominant technology for  $\text{H}_2$  production, constituting around 75% of global output [20][21][22]. Recent advancements in SRM focus on bio-alcohols, extending its carbon-neutral applications to methanol, ethanol, propanol, propanediol, butanol, ethylene glycol, and glycerol [23][24][25]. Distinctions between SRM, POM, and DRM lie in the oxidant used, reaction kinetics, energy requirements, and the syngas ratio ( $\text{H}_2/\text{CO}$ ). Though, DRM is the most promising among SRM, POM, and DRM since it utilizes abundant GHGs ( $\text{CO}_2$  and  $\text{CH}_4$ ) and provides a cost-effective method for reducing net emissions into the environment. DRM is economically favorable, allowing simple gas separation and offering a versatile syngas ( $\text{H}_2/\text{CO}$ ) ratio for oxygenated chemicals and higher hydrocarbons via FTS [26]. It's a viable option for clean fuel production from biogas ( $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ ) and holds potential for energy storage [27][28]. Extensive research has been conducted on the DRM process, with studies focusing on various factors such as the effects of active metals, preparation methods, supports, promoters, and calcination temperatures, all yielding satisfactory results. These investigations have primarily centered on addressing challenges such as the sintering of active metals due to the catalyst's poor thermal stability, undesirable  $\text{CO}$  disproportionation reaction (Boudouard reaction), and coke formation-induced catalytic deactivation [29]. The energy-intensive nature of DRM presents two challenges for the catalyst: sintering of the active phase and carbon poisoning caused by multiple side reactions [30]. The occurrence of the Reverse water gas shift (RWGS) reaction as a side reaction during the process increases the catalyst's sensitivity to metal sintering [31]. Meanwhile, other side reactions, such as  $\text{CH}_4$  cracking,  $\text{CO}_2$  and  $\text{CO}$  hydrogenation, and the Boudouard reaction, produce carbon on the catalyst surface, leading to

catalyst deactivation and obstruction of the active sites [26]. The modification of the catalyst's structure is considered to affect its catalytic activity.

Outstanding DRM performance has been observed among various noble metal-based catalysts, including Rh, Ru, Pt, Pd, and Ir [32][33]. Although noble metal-based catalysts have shown incredible DRM performance, they are neither viable nor sustainable from an industrial perspective. This is because they may be more susceptible to sintering at high temperatures. Three critical elements must be studied in order to maximize the use of DRM at the commercial level; (i) improve the activation of  $\text{CO}_2$  and  $\text{CH}_4$ , (ii) a thorough understanding of the chemical routes and processes leading to  $\text{H}_2/\text{CO}$  production, (iii) and strategies to prevent catalyst deactivation reactions [34][18]. According to literature, the utilization of DRM was not the only operating condition under which coke formation and related harmful consequences may have occurred [35]. However, Ni-based catalysts have been extensively tested as an alternative to costly and inaccessible noble metal catalysts. Ni has shown comparable activity to noble metals, and it is relatively inexpensive and abundant. However, utilizing Ni-based catalysts led to sintering and coking deactivation, resulting in low catalytic stability during the DRM process [33], which constrained the viability of the Reverse Boudouard reaction [21]. As they have a relatively low temperature ( $691\text{ }^\circ\text{C}$ ), Ni particles tend to quickly combine by sintering at high reforming temperatures ( $> 500\text{ }^\circ\text{C}$ ) [18]. Therefore, a Strong metal-supporting interaction (SMSI) is necessary to inhibit carbon growth and prevent the agglomeration of nickel species at elevated temperatures [18][30]. Therefore, catalytic modifications are essential to enhance stability and performance in DRM reactions due to carbon deposition. Additionally, optimizing the

active catalyst involves studying properties like dispersion, Metal-support interaction (MSI), and active surface, influencing metallic phase and acid-base centers. Typically, the Ni-C bonds that form during the intermediate phase of adsorbing methyl groups, generated by CH<sub>4</sub> activation, onto the catalyst surface, must be weakened to prevent carbon deposition. The effective improvement of catalytic stability is achieved by introducing oxygen atoms into the catalyst surface. When the oxygen produced by the surface of oxide interacts with the carbon that has been deposited, CO is released, preventing more carbon backlog [36]. By adding more metals, Ni catalysts' surface properties can also be changed, which increases DRM activity [37][38]. Modifying the catalytic support minimizes coke deposition, enhances initial activation, and improves overall performance. Catalyst synthesis method optimization leads to superior catalytic performance, increased stability, and reduced coke formation during the reaction.

According to the literature, selecting suitable supported materials, such as metal oxides, and using suitable synthesis methods are vital for enhancing the catalytic physicochemical properties. This approach facilitates the enhancement of SMSI, thereby improving the Ni-based materials for carbon deposition [39][40]. Furthermore, the supported materials with high heat resistance and adequate surface areas could effectively maintain Ni active sites. This stabilization aids in inhibiting carbon formation and preserving high performance during the reaction [41]. Hence, many metal oxides (e.g., MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, ZrO<sub>2</sub>, and CeO<sub>2</sub>) are frequently employed as supported materials due to their redox properties and oxygen mobility [42]. Among them, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are the most commonly used supported materials due

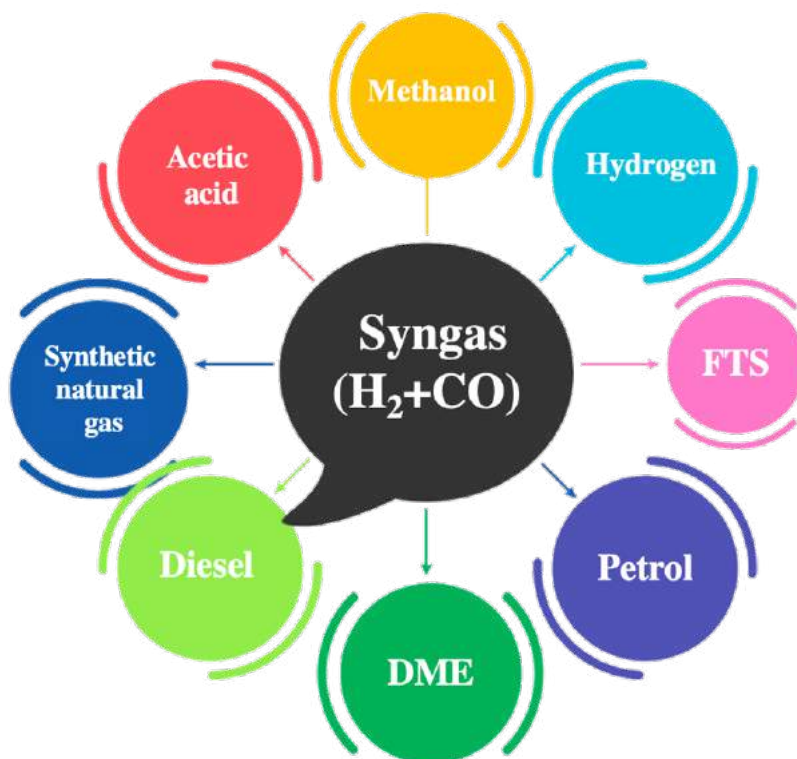


Figure 1.1: Applications of syngas for the synthesis of value-added chemicals.

to their high surface areas and improved textural properties [43]. In particular, the use of mesoporous  $\text{SiO}_2$  supports [44] or capsules [45] to contain metal particles is a frequently used method for regulating their dispersion and protecting them from sintering. This approach takes advantage of a physical barrier, especially when the metal particles are fixed within the oxide support itself. Recently, a number of mesoporous hexagonal materials containing  $\text{SiO}_2$  have been developed, most notably MCM-41 and SBA-15 [46]. While large inner surfaces on MCM-41 and SBA-15 may have provided numerous sites for active metal adhesion, their pore channels with front-rear apertures limited the availability of reactants [46]. By producing mesoporous silica as fibrous KCC-1, Polshettiwar et al. [47] successfully addressed the problem of restricted reactant accessibility. As a spherical entity with fibers extending in all directions, the

KCC-1 fibrous structure contributes to its exceptional activity. It has been found that supported materials with Lewis acidity tend to promote coking, which may be mitigated by incorporating additives with alkaline properties. Surface basicity is an important factor that influences carbon deposition during catalytic reactions [48]. According to the literature, the presence of Lewis basic sites on a metal oxide support can reduce or even prevent carbon formation when the metal is supported [49][50]. These modifications boost the resistance to carbon deposition, prevent poisoning, and promote dispersion of the metal particles during reaction [51]. One of these metal oxides is  $\text{La}_2\text{O}_3$ , a rare earth element that is economically viable and finds extensive application as supports, catalyst additives, and structure stabilizers for various applications.  $\text{La}_2\text{O}_3$  is recognized for its pronounced alkalinity, which facilitates reactions with  $\text{CO}_2$  to produce  $\text{La}_2\text{O}_2\text{CO}_3$ , which is considered a good intermediate of  $\text{La}_2\text{O}_3$  to reduce the coke deposition. In addition,  $\text{La}_2\text{O}_3$  is commonly employed as a promoter in catalytic systems due to its ability to enhance various catalyst properties, such as surface basicity and MSI. Montero et al. [51] conducted a study utilizing  $\text{La}_2\text{O}_3$  as a promoter to examine the mechanism of carbon formation on  $\text{Ni}/\text{La}_2\text{O}_3\text{-}\alpha\text{-Al}_2\text{O}_3$  catalyst. The inclusion of  $\text{La}_2\text{O}_3$  allows for the tuning of the support’s surface basicity, effectively suppressing the formation of  $\text{C}_2\text{H}_4$ , which acts as a precursor for carbon formation. Additionally, Singh et al. [52] discovered that the activity of  $\text{Ni}/\text{La}_2\text{O}_3$  catalysts is strongly affected by the structure and shape of the parent Nanoparticles (NPs). They found that parent NPs with high aspect ratios, such as rods, exhibited particularly favorable characteristics. Another metal oxide is  $\text{ZnO}$ , which also serves as a support due to its high melting point, allowing for the formation of a relatively large surface

area at elevated temperatures [53][39]. Numerous studies have demonstrated that the addition of ZnO contributes unique physicochemical properties to DRM catalysts [54][55]. For instance, Anjaneyulu et al. [56] observed that the existence of Zn influenced the metallic phase of Ni/ZnO-Al<sub>2</sub>O<sub>3</sub>, with the growth of a Ni-Zn alloy positively affecting stability by limiting coke production. Similarly, Chen et al. [57] found that ZnO loading increases catalytic efficiency, reduces CO selectivity, and prevents activity loss. The Zn content significantly impacts the Ni-based catalysts, thereby limiting coke formation and improving catalyst stability. Furthermore, Park et al. [58] studied the Zn effect as a promoter for improving the effectiveness of Co/ZrO<sub>2</sub> catalysts and discovered that the formation of Co-Zn alloys suppresses metal oxidation, resulting in increased catalytic stability. Besides, Nataj et al. [54] carried out a study where they developed Ni/ZnO-Al<sub>2</sub>O<sub>3</sub> with various Zn amounts for DRM. They investigated the impact of these catalysts on various physicochemical properties. They found that the addition of Zn decreased the surface area, enhanced Ni reduction, and weakened MSI.

Nonetheless, an essential aspect of heterogeneous catalytic systems involves exploring the fabrication of notably practical supported metallic catalysts characterized by way of a high dispersion of NPs. In this context, we have developed a catalytic system for DRM using a mixed metal oxide support: silica-lanthanum oxide (SLF) and silica-zinc oxide (SZF) to support Ni-based catalysts. This was achieved through the utilization of microemulsion and impregnation methods. Our objectives were to enhance the catalyst's basicity, inhibit carbon formation on SiO<sub>2</sub> by integrating La<sub>2</sub>O<sub>3</sub>, and improve H<sub>2</sub> selectivity, reduce CO selectivity, minimize activity loss, and enhance stability during the DRM reaction through ZnO incorporation. To the best of

our knowledge, there have been no previous reports on the synthesis of SLF support with this type of morphological structure and synthesis method for DRM. Our primary objective is to investigate the influence of the morphology and textural properties of the SLF and SZF support on Ni active metal and explore the impact of Ni loading on the SLF for DRM. The SLF structure can increase the dispersion of the Ni particles due to the presence of the fibrous shell and the enhanced surface area, and limit the agglomeration of Ni particles. Therefore, carbon deposition can be limited and the overall performance of DRM can be improved.

## CHAPTER 2

# LITERATURE REVIEW

It is well known that the physicochemical properties of the catalyst, such as Oxygen vacancies ( $O_{Vs}$ ), MSI, particle size, metal dispersion, acidity/basicity, reducibility, and surface area, can be modified to increase the DRM catalytic activity. The physicochemical properties of the catalyst and its constituents (supporting materials, active metals, and promoters) interact synergistically during the DRM process, along with parameters such as synthesis method and reactor type, as revealed in Figure 2.1.

## 2.1 Physicochemical Properties of DRM Catalysts

### 2.1.1 Particle size and metal dispersion

It is widely known that different metal species with variable sizes demonstrate various catalytic behaviors for various heterogeneous catalytic processes. Hence, one of the fundamental catalytic features to enhance the DRM reaction is increasing the active sites of catalysts by controlling the size of the metal particles. The percentage of substance atoms that are exposed to the surface is known as metal dispersion. In

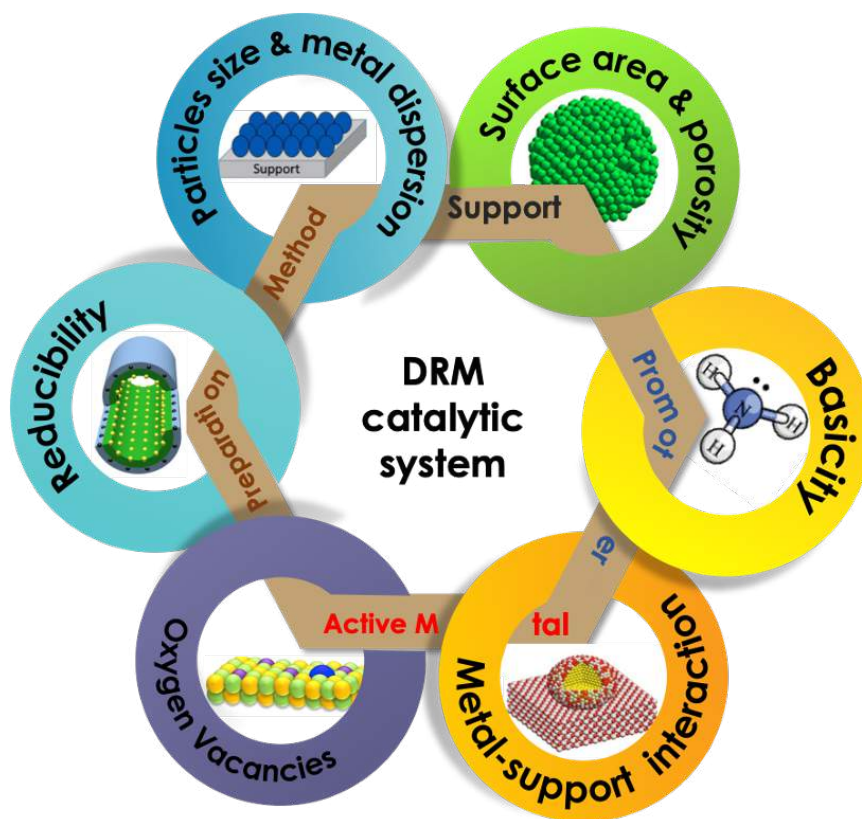


Figure 2.1: catalytic features for highly effective and active DRM catalytic systems.

heterogeneous catalysis, achieving high metal dispersion is crucial for enhanced activity, as only surface-exposed atoms can actively participate in catalytic reactions. As the crystalline diameter decreases to around 0.1 nm, dispersion begins to increase and eventually approaches unity. Common methods for analyzing metal particle size and dispersion on catalysts include Energy-Dispersive X-Ray (EDX) mapping analysis, Transmission electron microscopy (TEM), H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR), chemisorption, and Temperature programmed oxidation (TPO) [59][60].

The Ni particle size, dispersion, and MSI of the fully reduced catalysts were all significantly influenced by the oxide-phase origin of the Ni metal in Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. These effects were easily controlled by adjusting the calcination temperature of the sample. For example, Kwon et al. [61] examined the catalytic behavior of various Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for the DRM, utilizing diverse sources of Ni metal, including NiO as well as non-stoichiometric and stoichiometric NiAl<sub>2</sub>O<sub>4</sub>. It was observed that as the size of Ni particles decreased, the dispersion of Ni metal increased from 3.0% to 5.4%. The decrease in *Brunauer–Emmett–Teller*(*BET*) Surface area was attributed to the loss of small pores, which resulted in the sintering of the Al<sub>2</sub>O<sub>3</sub> support as the calcination temperatures were elevated. They established that none of the reduced catalysts had any oxidic Ni precursor and that various Ni particle sizes (dispersion) developed depending on the source of a Ni metal precursor. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst obtained by fully reducing the stoichiometric NiAl<sub>2</sub>O<sub>4</sub> precursor at elevated temperatures exhibited a higher dispersion of Ni particles, with smaller sizes and stronger interactions with Al<sub>2</sub>O<sub>3</sub>. Consequently, this catalyst demonstrated improved stability and activity, resulting in the formation of relatively lower amounts of graphitized

carbon deposit. Furthermore, Qin et al. [62] synthesized catalysts with nanoscale Ni particles embedded in activated carbon by the EDTA-assisted impregnation method. According to the experimental findings, adding EDTA increased Ni particle dispersion and reduced Ni particle size. When the Ni/EDTA ratio was raised from 1:0 to 1:3, the size of the Ni particle was considerably reduced from 18.23 to 4.57 nm. After a 72-h DRM reaction, the catalytic performance of Ni15-AC-catalytic exhibited CH<sub>4</sub> and CO<sub>2</sub> conversion rates of 90.05% and 96.28%, respectively, under an operational condition of 850 °C. Furthermore, following the stability test, the size of the Ni particles experienced a slight increase from 4.57 nm to 5.94 nm, and no manifestation of NiO was observed. Notably, when the EDTA/Ni ratio was increased from 0:1 to 1:1, the size of the Ni particles was significantly reduced from 16.54 nm to 7.61 nm, demonstrating the beneficial effect of EDTA-assisted impregnation in the formation and dispersion of nanoscale Ni particles. In addition, Liu et al. [63] conducted a study to examine the dispersion of Ni in the 2.5Ni(IM)-Syn catalyst by evaluating H<sub>2</sub> chemisorption. They observed that under alkaline conditions, Ni species attached to the mesoporous Al<sub>2</sub>O<sub>3</sub>. The results showed that the Ni dispersion in the 2.5Ni(IM)-Com and 2.5Ni(IM)-Syn catalysts was higher than 2.25% and 3.77%, respectively. This suggests that the alkaline environment promoted higher reactivity, leading to enhanced dispersion of Ni species. It was proposed that factors other than the large specific surface area of mesoporous Al<sub>2</sub>O<sub>3</sub> may also contribute to the increased dispersion of Ni species. Besides, Chai et al. [64] synthesized a perovskite catalyst using the combustion method, resulting in a bimodal size distribution of Ni particles. Their findings showed that small Ni particles stayed active, while larger ones deactivated

from sintering and carbon deposition. Under severe conditions for 100 h of reaction, the bimodal catalyst exhibited only 3.0% carbon deposition compared to the catalyst consisting solely of large Ni particles, which had 4.8% carbon deposition. The bimodal Ni catalyst demonstrated higher resistance to coke formation compared to the catalyst with fewer small particles. Hou et al. [65] found that adding Rh as a promoter enhanced catalytic activity and reduced coke deposition during DRM over Ni-supported  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and mesoporous Al<sub>2</sub>O<sub>3</sub> at 800°C. On  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support, CO<sub>2</sub> and CH<sub>4</sub> conversions increased with lower Rh loadings but decreased significantly when Rh concentration exceeded 1 wt.%. In the mesoporous system with higher Rh dispersion (100%), conversion increased linearly with increasing Rh amount from 0.5 to 5 wt.%. Rh suppressed coke deposition, with no coke observed when the Rh/Ni ratio exceeded 0.1, indicating synergy between Rh and Ni facilitated by Al<sub>2</sub>O<sub>3</sub>'s mesoporosity.

### 2.1.2 Surface area and porosity

The influence of total surface area on reaction rates in chemical reactions is widely recognized. Smaller sizes of catalyst components lead to a greater particle surface area, thereby reducing the surface energy of the catalyst. Numerous studies have indicated that analytical models considering size-dependent surface energy have a profound impact on catalytic activity [66][67]. Mesoporous materials exhibit notable characteristics such as a high specific surface area, homogeneity, and interconnected porosity, rendering them suitable for diverse catalytic applications. While maintaining these exceptional properties at high temperatures used to be challenging, recent advancements in synthesis techniques have enabled their utilization. It has been observed

that enhancing the specific surface area, resulting in a higher number of CO adsorption sites per gram, can enhance the catalytic performance of DRM. The catalyst's elevated surface area and porosity facilitate the entry of CO and O<sub>2</sub> molecules into its pores, providing a larger number of active sites and enabling the catalyst to exhibit effective catalytic activity for DRM. To assess surface area and porosity, the N<sub>2</sub>, CO<sub>2</sub>, or H<sub>2</sub> adsorption method is commonly employed, utilizing the BET theory [68]. Due to its large specific surface area, well-organized mesoporous pores, and strong thermal stability, mesoporous Al<sub>2</sub>O<sub>3</sub> is commonly used in DRM applications. This gives the active ingredients a higher dispersion and more stable structure. Nonetheless, the presence of carbon deposition can lead to the obstruction of mesoporous pores, adversely affecting the catalyst's activity. Adjusting the catalyst's surface area and pore size is crucial for evenly dispersing active components and improving the diffusion rate of reactant and product molecules [69].

Lyu et al. [69] synthesized a bimetallic Ni-Co catalyst with a bimodal pore structure to investigate its impact on catalytic performance and stability in DRM. The addition of Co significantly decreased the specific surface area of the catalyst and reduced the volume of the pores. Co was employed as a substitute metal to modify the overall specific surface area. The decrease in specific surface area and pore volume may result from the integration of smaller Ni-Co particles into the Al<sub>2</sub>O<sub>3</sub> support structure. When the Co/Ni ratio was minimal, there was minimal alteration in the mesopore diameter of the samples. Both the specific surface area and pore volume increased with higher Co/Ni ratios, suggesting that the addition of Co also contributed to the catalysts' specific surface area. Using varying Ni loadings (5–15 wt.%), spher-

ical mesoporous Ni/FSA catalysts were synthesized and catalytically tested by Owgi et al. [70]. The FSA catalyst has a surface area of 334.92 m<sup>2</sup>/g, while the 12.5Ni/FSA catalyst exhibits the highest specific surface area of 645 m<sup>2</sup>/g and pore volume of 1.91 cm<sup>3</sup>/g. Increasing Ni content from FSA to 12.5Ni/FSA expands the surface area. The average pore size and  $S_{BET}$  have a direct relationship; the large specific surface area correlates with the small pore sizes. This reveals the small particles of Ni deposited within the pores; the addition of 15% Ni, on the other hand, leads to a decline in surface area. The optimal Ni value for preventing coke deposition on the FSA and enhancing catalytic performance was found to be 12.5 wt.% Ni. With various Ni loadings over MCM-41 mesoporous, Liu et al. [71] studied the catalytic activity for DRM by H<sub>2</sub> chemisorption. They reported that Ni/MCM-41 was more stable than common Ni/SiO<sub>2</sub> due to the stabilization of active species dispersion by the SiO<sub>2</sub> matrix and Ni ions. The mesoporous materials that were produced have excellent thermal stability and desirable textural characteristics. This characteristic was particularly important in increasing the accessibility of the Ni active centers and stabilizing the Ni NPs via the confinement effect.

### 2.1.3 The acidity and basicity

Surface acidity and basicity are crucial in the DRM process. They are supported by either the active metal, promoter, or the catalyst support. NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD) and CO<sub>2</sub>-temperature programmed desorption (CO<sub>2</sub>-TPD) are commonly used techniques to measure acidity and basicity. It has been noted that acidity plays a vital role in preventing the dissociative chemisorption

of  $\text{CO}_2$ , thus reducing coke formation [69]. Research indicates that the catalyst's basicity improves  $\text{CO}_2$  adsorption, facilitating carbon deposit gasification and inhibiting their expansion and graphitization. In the presence of nearby Ni and other active metal particles, chemisorbed  $\text{CO}_2$  becomes activated on the catalyst support, forming an intermediate carbonate species. This intermediate carbonate species then interacts with  $\text{CH}_4$  molecules, leading to the synthesis of CO [72][73]. The catalyst's properties attract acidic  $\text{CO}_2$  molecules, enhancing  $\text{CO}_2$  surface coverage and reducing carbon deposition via the Boudouard reaction [18]. A higher concentration of strong Lewis acid sites promotes extensive carbon deposition, resulting in decreased catalytic performance. Therefore, to enhance activity and stability, it is beneficial to generate weak Lewis acid sites and hydroxyl group ions on the catalyst support. These properties are influenced by the structure and nature of the catalyst support and promoters employed. In the case of an acidic catalyst, the accumulation of dehydrogenated carbon on the catalytic surface obstructs the active sites responsible for  $\text{CO}_2$  adsorption, thereby hindering the dissociative chemisorption of  $\text{CO}_2$  and leading to catalyst deactivation [74].

To investigate the influence of catalyst acidity and basicity in the DRM process, Jun Ni et al. [75] conducted a study on borated  $\text{Al}_2\text{O}_3$ -supported 5 wt.% Ni catalysts with varying  $\text{B}_2\text{O}_3$  loadings (0, 1, 5, and 10 wt.%). The researchers observed that the presence of strong Lewis acid sites on the 1 wt.% and 10 wt.%  $\text{B}_2\text{O}_3$ -loaded Ni catalysts resulted in significant carbon deposition, leading to a reduction in catalytic activity and stability. In contrast, the introduction of weak Lewis acid sites and hydroxyl groups on the 5 wt.%  $\text{B}_2\text{O}_3$ -promoted Ni catalyst facilitated the removal of

coke deposits and enhanced the stability of the catalysts. Promoters are strongly believed to effectively mitigate carbon deposition through the following mechanisms: i) by modifying the catalyst's basicity, they increase the capacity for CO<sub>2</sub> adsorption and activation, and ii) they enhance the dispersion of Ni particles. At temperatures between 200 °C and 400 °C, basic site strengths are often classified as weak, medium, and strong. Furthermore, Abasaeed et al. [76] improved the performance of mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Ni catalyst by incorporating it as a promoter for the DRM. It is well recognized that basicity facilitates CO<sub>2</sub> adsorption, while acidity enhances CH<sub>4</sub> dissociation. Following an optimal loading, the delicate balance between acidic and basic sites was disrupted, resulting in increased carbon deposition at 7.0 wt.% Ni and reaching its maximum at 9.0 wt.% Ni. However, when the WO<sub>3</sub> promoter was loaded up to 5.0 wt.%, an appropriate equilibrium between acidic and basic sites was achieved, leading to efficient carbon removal and improved coke resistance. The 5.0 wt.% WO<sub>3</sub>-promoted catalyst demonstrated stable and reducible NiAl<sub>2</sub>O<sub>4</sub> and NiWOAl species with a moderate density of basic sites and a maximum density of acidic sites. After 7.5 h of continuous operation, this catalyst displayed strong catalytic activity, converting 79% of CH<sub>4</sub> and 83% of CO<sub>2</sub>. However, exceeding 5.0 wt.% WO<sub>3</sub> overload resulted in decreased catalyst stability, increased carbon deposition, and decreased CH<sub>4</sub> and CO<sub>2</sub> conversions, most likely due to WO<sub>3</sub> covering active sites. Zeolites are known for their amphoteric nature, possessing both acidic and basic sites. The three ordered structures, namely Al sites and non-framework Al sites, are commonly referred to as Lewis acid sites. Despite oxygen being structurally basic, its interaction with the neighboring Al (Si-O-Al oxygen) leads to strong basicity due

to the substantial negative charge on the oxygen atoms. Within zeolites, Lewis acids play the role of charge-balancing cations; Lewis acidity involves electron donation, whereas Lewis basicity involves electron acceptance. The intrinsic properties of catalysts play a critical role in the catalytic efficiency of the DRM reaction, as they need to withstand the acidic nature of CO<sub>2</sub> [77]. Typically, catalysts with high basicity are expected to slow down the desorption process by forming strong interactions with pyrrole molecules on the surface. This characteristic suggests that the strength of basicity in the samples can be ranked as Ni/FSA > FSA > Si-Al > Ni/Si-Al. Additionally, previous research has demonstrated that the intrinsic quality of FSA is closely associated with O<sub>Vs</sub> present in dendrimeric fibers and surface imperfections. The generation of unpaired electrons from the formation of O<sub>Vs</sub> leads to a pronounced Lewis basicity on the catalyst surface. Consequently, the O<sub>Vs</sub> sites in Ni/FSA catalysts are considered crucial for enhancing CO<sub>2</sub> adsorption during the DRM reaction [78].

#### **2.1.4 Metal-support interaction**

SMSI is generally characterized as a cohesive chemical and physical interaction occurring between the metal and the support material. The term SMSI was first used in 1978 following Schwab and Koller’s study on Ag with ZnO semiconductor catalyst in the late 1960s [79]. With the SMSI principle, the significance of the interaction between metal and support has now been well demonstrated in all catalytic processes [79][80]. During the process of DRM, two distinct types of interactions occur on the catalysts: MSI, and the combined effect of bimetals and the support interaction. SMSI

acts as a resistance against sintering, leading to a notable enhancement in the active metal dispersion. Consequently, the active species can maintain a relatively small size; bimetals collaborate synergistically to enhance dispersion and provide additional active sites. Additionally, SMSI prevents the onset of Hüttig and Tamman temperature limitations, which are indicative of sintering initiation [73]. Using SMSI may offer the potential to enhance the catalytic properties of reactions, such as the oxidation of CO [81][82]. A notable manifestation of SMSI is the metal particle encapsulation by minimizing oxide supports like  $\text{CeO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_3$ ,  $\text{TiO}_2$ , and others. This phenomenon arises from the combination of active metals with high surface energies and low-surface-energy oxides (e.g., Pt and Pd with  $\text{CeO}_2$  and  $\text{TiO}_2$ ), resulting in an overall reduction in surface energy [83][84]. Researchers employ various techniques, including X-ray absorption spectroscopy (XAS), Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), Scanning probe microscopy (SPM), TEM, and  $\text{H}_2$ -TPR, to investigate SMSI. Modulating SMSI in catalysts to enhance CO oxidation involves effective modifications in the electronic and structural properties of the catalyst surface. It is widely recognized in the literature that establishing a favorable MSI is crucial, particularly at elevated temperatures in DRM, as it promotes catalytic activity and mitigates catalyst deactivation caused by coke formation and active metal sintering [85]. The supports, particularly for Ni-based catalysts, are principally responsible for controlling the DRM reaction since they commence the activation and adsorption process. In a bi-functional DRM reaction pathway,  $\text{CH}_4$  is activated on the active metal's surface, while  $\text{CO}_2$  is activated on either a slightly basic ( $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ) or an acidic ( $\text{Al}_2\text{O}_3$ ) support. Catalysts supported on silica, on the other hand, take a

mono-functional approach, with both  $\text{CH}_4$  and  $\text{CO}_2$  activation occurring on the active metal surface [86]. The development of thermal resistance to temperature limitations of Hüttig and Tamman in catalysts with SMSI serves as an indicator of the temperature at which sintering commences. At elevated temperatures during DRM, SMSI facilitates active metal dispersion, ensuring its uniform and minute size [87][88]. Agglomeration is hindered by the increased temperature required for a metal to separate and merge with an adjacent metal particle; a phenomenon attributed to the strength of the metal-support contact. It is thought to be more suited for bimetallic catalysts than acidic/basic supports because it has less contact between the active metal and the inert support. This expectation is based on the belief that it will improve metal-metal interaction [86]. The control of active metal localization within the support skeletal structure was achieved through catalyst manufacturing techniques, providing insights into the underlying interaction. Various synthetic procedures have lately been utilized with different degrees of success to generate catalysts with higher coke and sinter resistance by immobilizing Ni particles. Most notably the formation of alloys with promoters; confinement in the structure of mesosilica shell; Polyol-assisted fixation in  $\text{SiO}_2$  mesoporous channels; sublimation-deposition; and confinement of aerogel [89][85]. Despite their excellent coke resistance, noble metal catalysts have limitations because of weak MSI. When subjected over a lengthy period to reaction conditions, noble metal sintering, which results from the metals' simple delocalization on the support surface and facilitation of their aggregation, reduces the metals' catalytic activity and stability, as proved by Beltrán et al. [90] study. Which Rh was supported on pure oxides and modified  $\text{ZrO}_2\text{-Al}_2\text{O}_3$  using the impregnation method. The objective was

to investigate the impact of the MSI on the reaction rate of DRM. The Rh-support interaction was influenced by the coverage of  $\text{Al}_2\text{O}_3$  with  $\text{ZrO}_2$  and the nature of the  $\text{ZrO}_2$  phase in the grafted supports. Higher coverage of  $\text{Al}_2\text{O}_3$  with  $\text{ZrO}_2$  resulted in a weaker Rh-support interaction. However, the interaction between Rh and the monoclinic phase of  $\text{ZrO}_2$  was found to be weaker compared to the tetragonal phase, which became more dominant as the  $\text{ZrO}_2$  loading in the grafted supports increased. Consequently, the Rh-support interaction strengthened with higher  $\text{ZrO}_2$  content.

### 2.1.5 Oxygen vacancies

The concept of  $\text{O}_{Vs}$  and their interaction with gases and solid surfaces was initially introduced by Tompkins et al. in 1960 [91].  $\text{O}_{Vs}$  are essential point defects commonly observed in metal oxide supports. These vacancies can be deliberately manipulated through the synthesis of catalysts by subjecting them to elevated temperatures under a reduced atmosphere. This process allows for the controlled formation and modification of  $\text{O}_{Vs}$  in the catalyst structure [92]. The catalyst support possesses a unique characteristic that facilitates the storage and release of oxygen under specific conditions. Under oxidizing conditions, the support effectively stores oxygen, while under reducing conditions, it releases the stored oxygen, leading to the development and filling of  $\text{O}_{Vs}$  [93]. The presence of active lattice oxygen atoms and  $\text{O}_{Vs}$  has been found to significantly enhance the catalytic efficiency. These oxygen species contribute to improved electrical and chemical properties, facilitating the nucleation and growth of metal NPs. As a result, the catalytic system demonstrates high performance and enhanced activity [94]. The majority of the materials used as supports and promoters

have significant Oxygen storage capacity (OSC), and when paired with active metals, they boost oxygen atom mobility through the crystal lattice and encourage the formation of  $O_{Vs}$  [69]. Oxygen defects have the potential to activate and dissociate  $CO_2$ , generating mobile oxygen on the catalyst surface. This mobile oxygen reacts with carbon to form CO and intermediate carbonate species, significantly reducing coking. Its presence plays a crucial role in facilitating the in-situ oxidation of stored carbon, leading to CO production [95]. A high concentration of oxygen species intensifies the surface carbon gasification process, effectively preventing carbon formation during the DRM. The enhancement of the mobile oxygen proportion on the catalyst's surface not only promotes surface carbon gasification during DRM but also facilitates FTS and CO oxidation, effectively mitigating carbon formation and deposition [96]. In a study conducted by Gao et al. [59], the impact of hierarchically  $CeO_2$  support on the DRM performance of Ni/ $CeO_2$  catalysts was investigated. The Ce 3d XPS spectra analysis revealed eight distinct peaks, indicating the coexistence of  $Ce^{3+}$  and  $Ce^{2+}$  species with a reversible redox cycle.  $CeO_2$  lattice oxygen can dissipate, forming intrinsic  $O_{Vs}$ , which are crucial for facilitating  $CO_2$  adsorption and activation, thereby enhancing catalyst activity. The O 1s XPS spectrum was divided into three bands:  $O_\alpha$ ,  $O_\beta$ , and  $O_\gamma$ . Elevated lattice oxygen oxidation state ( $O_\alpha$ ) caused a surge at low binding energy (529.4 eV), while  $O_{Vs}$  ( $O_\beta$ ) exhibited a comparable impact on desired surface-active oxygen, observed at higher binding energy (531.4 eV). The chemisorbed oxygen on the catalyst surface ( $O_\gamma$ ) was centered at 533.0 eV and included bound water hydroxyl radicals. The presence of a NiO peak at approximately 854-855 eV indicated the dispersion of NiO on the sample surface, suggesting mild MSI. Notably, Ni/ $CeO_2$ -D with

the highest Ni/CeO<sub>2</sub> ratio (1.78) displayed a stronger MSI, leading to enhanced CH<sub>4</sub> adsorption/dissociation and catalytic activity. The Ni 2p<sub>3/2</sub> spectra analysis revealed peaks for Ni<sup>0</sup> and Ni<sup>2+</sup> species at 852.7 eV and 855.6 eV, respectively. Ni/CeO<sub>2</sub>-D showed the highest percentage of the Ni<sup>0</sup> peak, indicating its greatest dispersity and smallest Ni NPs size.

Recently, investigation has focused on maximizing the presence of O<sub>Vs</sub> to enhance CO<sub>2</sub> activation and dissociation, leading to increased CO production. The search for catalyst supports with exceptional OSC and unique redox characteristics is still ongoing. These catalyst supports exhibit a high potential for retaining O<sub>2</sub> and facilitating the migration of the atoms of mobile oxygen to the surface. This promotes the carbon deposit oxidation and the vacancy formation on the supports, enabling efficient CO<sub>2</sub> activation. CeO<sub>2</sub> and CeO<sub>2</sub>-based catalysts have shown great promise as supports for CO<sub>2</sub> activation. Their high OSC, strong reducibility, increase of mobile oxygen pools, and formation of significant unoccupied sites contribute to their effectiveness. In another report, da Fonseca et al. [97] studied the relationship between O<sub>Vs</sub> and Ni crystallite size of the support with the deposition of coke rate over Ni/CeO<sub>2</sub> in the DRM process. By applying various Ni loading at different calcination temperatures, a significant crystallite size variation is produced. They discovered that as the calcination temperature increased, the size of the crystallite of Ni increased but the number of O<sub>Vs</sub> decreased. Because of the poor contact of metal support on these Ni particles, the O<sub>Vs</sub> of CeO<sub>2</sub> do not easily eliminate carbon from the Ni surface

### 2.1.6 Reducibility

Understanding the catalytic behavior of active oxide supports requires a thorough understanding of their surface reducibility. Tauster et al. [98] determined the relative reducibility of different metal oxides using  $\text{H}_2$ -chemisorption. They found SMSI properties, where catalytic reactivity was affected by support, metal stabilization, charge transfer, and metal particle encapsulation. The effects of SMSI and reducibility on catalytic efficiency have been the topic of considerable scientific study [99]. The most used method for examining the reducibility of catalysts is  $\text{H}_2$ -TPR. Several metal oxide-supported Au catalysts ( $\text{Au}/\text{Al}_2\text{O}_3$ ,  $\text{Au}/\text{TiO}_2$ ,  $\text{Au}/\text{ZnO}$ , and  $\text{Au}/\text{ZrO}_2$ ) were examined by Widmann et al. [100] for CO oxidation. The  $\text{O}_{Vs}$  and the reduction potential of the support material were strongly associated with the catalytic efficiency, indicating a specific effect of the support and its obvious involvement in the reaction. Before the catalytic reaction, DRM undergoes an activation phase converting initial oxides to a catalytically active metallic phase. Following this conversion, DRM enters an active state. The extent of reduction indicates the number of active sites. Strong interactions between supports and active metals may sometimes hinder the reaction by reducing reducibility and limiting active site formation. Due to their affordability and availability, metals like Ni and Co supported by materials like  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{ZrO}_2$  are some of the most used catalyst systems. Nevertheless, they are primarily extremely active at high temperatures and have a high potential to deactivate via coking. Many studies have demonstrated that combining platinum group metals like Pt, Ru, or Rh with Ni-based metals can improve their catalytic performance

(reducibility, activity, and stability) [101]. The effectiveness of Ru-Ni-Mg/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts for DRM at low temperatures (mainly 450-510 °C) was investigated by Sokefun et al. [102]. They demonstrated that metal chemisorption and reducibility are influenced by metal loading, metal-metal interactions, and MSI. Ru and Ni, the two catalyst active metals, significantly affected the reforming activity of the samples and the reducibility of the support material (CH<sub>4</sub> activation). They found that the solid NiO-MgO solutions in the Ru-Ni-Mg-CZO samples increased in surface CeO<sub>2</sub> and NiO reducibility as Ru loadings increased. The active phase of DRM is typically considered the metallic transition state. An activation step initiates the catalytic reaction to convert initial oxide phases into the catalytically active metallic phase. The number of available active sites is influenced by the level of decrease. In some instances, excessively strong contact between the active metals and the supports led to inactive phase development or poor reducibility, which prevented the establishment of active sites. Gadalla and Bower [103] noted that the breakdown of the catalyst structure was caused by the synthesis of NiAl<sub>2</sub>O<sub>4</sub> spinel in Al<sub>2</sub>O<sub>3</sub>-supported Ni catalysts. Pham et al. [104] investigated the effects of rare-earth elements on Co<sub>3</sub>O<sub>4</sub> reducibility using H<sub>2</sub>-TPR. Both Co reducibility and dispersibility were shown to improve with the addition of these rare-earth metals. Doping MgO with additional additives may change how NiO and MgO interact, adjusting NiO reducibility. To increase the reducibility of the catalyst, CeO<sub>2</sub> [105] or ZrO<sub>2</sub> [106] could be added to the MgO support as a promoter to prevent the formation of (Ni, Mg)O solid solution. Structure-directing agents, like molten salts, can significantly influence the structural evolution of (Ni, Mg)O, determining whether well-defined crystals or segregated phases form during the

solid solution synthesis [107]. These methods for enhancing the reducibility of NiO are based on preventing the solid solution of (Ni, Mg)O from forming. These methods, however, forgo the benefits of producing potent NiO-MgO interactions. Azancot et al. [108] studied the reducibility of the Ni species in three synthesized catalysts by applying H<sub>2</sub>-TPR. The decrease of NiO species with varying degrees of contact with the support was observed in all of the catalysts in the temperature range between 300 and 750 °C. They determined the degree of reducibility from the area under the TPR profile by assuming the Ni<sup>2+</sup> as a reducible species which is converted to metallic Ni species. This indicates that at least some of the Ni in the latter catalysts is not being reduced, most likely as a result of the existence of the NiAl<sub>2</sub>O<sub>4</sub> spinel or the strong contact between NiO and MgAl<sub>2</sub>O<sub>4</sub>. It can be inferred that the MSI played a significant role in reducibility.

## 2.2 Development of DRM Catalysts

The optimal catalyst for DRM must be exceptionally stable and exhibit resistance to coke production. Consequently, the design of the catalyst has become extremely important. The design of any catalyst is determined by a number of variables, including the active metals, promoters and supports used, the synthesis method, and the reactor employed.

### 2.2.1 Supports

A catalyst usually consists of multiple components assembled to achieve the desired shape and structure. In designing a supported metal catalyst, the active metal is typically embedded within the support material. These support materials are essential functions in catalyst action. They maximize the surface area of active sites, allowing metallic compounds to disperse, thereby providing a High specific surface area (HSA) for customization of the catalyst's geometry to suit the reactor [109]. While supports do not possess much catalytic activity on their own, they provide essential thermal and mechanical stability while also combining with active metal sites throughout the process to improve catalytic effectiveness (a bi-functional mechanism). Given the extremely endothermic behavior and greater coke formation involved in DRM, the quantity of mechanical as well as thermal stability provided by the support is critical [110]. The reaction pathway following adsorption and activation is determined by the support, particularly for Ni-based catalysts.

Several types of supports have been developed and employed throughout the years to provide the appropriate amount of dispersion, mechanical strength, and thermal durability. For instance, Sokolov et al. [111] developed a series of supported Ni catalysts and tested them in a low-temperature DRM system. Ni/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst revealed the highest CO and H<sub>2</sub> yield as well as the best stability. The researchers carried out a more detailed investigation on the performance of mesoporous, non-structured, and macroporous La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts before and after Ni loading. The results indicated that the mesoporous support with Ni exhibited no significant change

in activity during 180 h Time-on-stream (TOS), while the nonstructured and macroporous  $\text{La}_2\text{O}_3\text{-ZrO}_2$  supports experienced deactivation due to the formation of coke layers on the catalysts and a NiO shell around Ni particles, not because of Ni sintering. The researchers attributed the better stability of Ni on the mesoporous  $\text{La}_2\text{O}_3\text{-ZrO}_2$  support to the greater interaction of the Ni particles with the support caused by a pore confinement effect. Combining Ni/ $\text{ZrO}_2$  with  $\text{La}_2\text{O}_3$  resulted in an increase in  $\text{H}_2$  production from 5% to 5.4%. Meanwhile, Song et al. [112] utilized mesoporous support (SBA-15) and microporous silica support beta in Ni catalysts for the DRM process. In contrast, the catalysts prepared through the impregnation approach, Ni/SBA-15, exhibited well-dispersed Ni NPs on both the Ni-SBA-15 and Ni-beta catalysts. These catalysts displayed excellent catalytic efficiency, achieving an approximately 89%  $\text{CO}_2$  conversion and an approximately 84%  $\text{CH}_4$  conversion at 700 °C, as well as nearly 100% conversions at 800 °C. The mesopores of Ni-SBA-15 provided secure deposition sites for Ni NPs, preventing sintering and carbon deposition. However, due to the smaller porosity of beta, it was challenging to incorporate Ni into the micropores, hampering ammonia evaporation. The catalytic activities of the catalysts in the DRM process were assessed across temperatures ranging from 600 to 800 °C.

### 2.2.2 Active Metal

Transition metals belonging to groups 8-10 of the periodic table are known for their high efficiency as active metals in the DRM reaction. These metals can be categorized as noble metals and non-noble transition metals. Researchers have extensively studied both categories when supported on catalysts to determine their effectiveness in the

DRM reaction. Notably, noble metals have demonstrated superior resistance to carbon production and higher activity levels [113]. In the DRM reactions, both non-noble metals such as Ni, Co, Cu, and Fe, as well as noble metals including Rh, Pd, and Pt), have been employed as catalysts. These metals are selected for their superior catalytic activity in the DRM process. When it comes to coke production, the order of reactivity can be generalized as  $\text{Ni} \gg \text{Rh} > \text{Ir}, \text{Ru} > \text{Pt}, \text{Pd}$ . This implies that Ni catalysts tend to promote higher coke production compared to other metals like Rh, Ir, Ru, Pt, and Pd. On the other hand, the activity order, taking into account the overall catalytic performance, is typically described as  $\text{Ru}, \text{Rh (maximum)} > \text{Ir} > \text{Ni}, \text{Pt}, \text{Pd}$ . This ranking suggests that Ru and Rh exhibit the highest activity among the metals considered, followed by Ir, Ni, Pt, and Pd [114]. Among the non-noble, Ni is often selected as the preferred active metal for the DRM reaction. This choice is attributed to several factors, including its relatively low cost [115], high catalytic activity [116], and widespread availability [117] compared to other metals in the same category [117]. Despite Ni exhibiting high catalytic activity comparable to noble metals in the DRM reaction, it is prone to rapid deactivation caused by carbon formation and sintering [114]. Consequently, both noble and non-noble metals have been employed as active metals in the DRM reactions, with noble metals occasionally serving as promoters [118]. The performance discrepancy between noble metals and non-noble metals in the DRM reactions can be attributed to the noble metals' ability to disperse on the catalyst support and maintain small particle sizes. This characteristic has a significant impact on the type and amount of coke produced during the reaction [119]. Researchers have explored various strategies to address deactivation issues. One

such strategy involves the formation of bimetallic catalysts by combining a noble or non-noble metal with another main metal [120][121]. This approach aims to mitigate the deactivation caused by excessive coke production while also reducing costs [18]. Additionally, bimetallic catalysts can lead to smaller metal particle sizes and improved dispersion, resulting in enhanced catalytic activity and stability [122].

### **2.2.3 Promoter**

The addition of promoters, such as alkaline and alkaline earth metals, is widely recognized as an effective approach to mitigate carbon deposition and sintering, thereby preventing catalyst deactivation in the DRM reaction [123][124]. These promoters play a crucial role in preventing the formation of carbonaceous species on the catalyst surface by modifying the catalytic properties of the active metal and the support, leading to improved catalytic performance and enhanced resistance to coke deposition [125]. The exact mechanisms by which these promoters inhibit carbon formation may vary depending on the specific reaction conditions and catalyst system. Nonetheless, their utilization has shown promise in reducing coke formation and maintaining the long-term stability of catalysts in the DRM process. The inclusion of a promoter, such as CaO, is believed to limit sintering and enhance catalytic performance. Specifically, when Ca is introduced as a promoter during the calcination of Al<sub>2</sub>O<sub>3</sub>-based Ni catalysts, it induces structural changes that impact the catalytic performance. At a structural level, the interaction between the promoter CaO and the support leads to improved resistance against sintering. This interaction between Ca and Ni promotes the formation of reducible Ni species. The concentration of Ca has a significant

influence on the conversion of  $\text{CO}_2$  and  $\text{CH}_4$  in the DRM reaction. Lower concentrations of Ca result in the strong formation of ionic oxides, leading to increased  $\text{CO}_2$  conversion. Additionally, at lower Ca concentrations,  $\text{CO}_2$  is attracted to the catalyst's surface, further enhancing  $\text{CH}_4$  conversion. Conversely, higher concentrations of Ca increase the electron density of Ni, resulting in a decline in both  $\text{CH}_4$  and  $\text{CO}_2$  conversions [109]. Ferrandon et al. [126] reported a novel approach to enhance the activity, stability, and coke resistance of Ni-based catalysts by introducing a submonolayer of promoters, with the goal to improve Ni dispersion, reducibility, and interaction with the modified support. A systematic and high-throughput approach was employed to explore 95 different combinations of Ni and promoters (B, Mg, Cu, Fe, Mn, Co, Sn, Zn, and V) on various oxide supports ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , and  $\text{TiO}_2\text{-MgO}$ ). The promoters were grafted onto the catalysts using an organometallic precursor followed by carbonization, and then the Ni was deposited using bis(N,N'-di-t-butylacetamidinato)nickel(II) as the metal source. The choice of the promoters and supports was guided by existing research that established their potential in reducing sintering and coke formation. B was discovered to be effective in promoting carbon removal and enhancing resistance against coking. Furthermore, Sun et al. [1] conducted a study to investigate the influence of the impregnation sequence of active metals and promoters. The results revealed that the addition of various alkaline-earth metals did not significantly affect the reduction profile of  $\text{Co}_3\text{O}_4$  to  $\text{Co}^0$  (see Figure 2.2 (I, II)). The initial small reduction peak observed around 300 °C was attributed to the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ , which can be easily further reduced to  $\text{Co}^0$ . This reduction peak could be attributed to both weak MSI and bulk metal oxides. The

peak observed around 450° C was associated with the reduction of  $\text{Co}^0$  to Co. Moreover, the reduction peaks at higher temperatures were ascribed to the less reducible Co-Ce bimetallic species. The basicity of the catalysts was evaluated using , as demonstrated in Figure 2.2 (II). The profiles of all catalysts exhibited multiple peaks. The peak around 150°C was assigned to the presence of weak basic sites on the catalysts. It was evident that the addition of promoters significantly increased the content of weak basic sites. However, the intensity of this peak was similar among catalysts promoted by different alkaline earth metals and prepared using different methods. The peak at approximately 450 °C corresponded to medium strength basic sites. Notably, the intensity of this peak was much stronger in the unpromoted catalyst, primarily due to the presence of hydroxyl groups on the surface of the carbon material.

## 2.2.4 Preparation method

The choice of synthesis method is a crucial determinant of the properties and catalytic activity of DRM catalysts. Each step of the preparation process, along with the quality of the precursors, significantly influences the characteristics of the catalysts. Therefore, the selection of a specific synthesis method for a catalyst is based on the desired physicochemical properties expected in the final material [127]. According to Arora and Prasad [128] different synthesis methods such as impregnation, co-precipitation, Sol-gel method (SG), surfactant-assisted and polyol and atomic layer dispersion methods can be used to prepare several types of catalysts for DRM reaction. These methods have an impact on the loading, dispersion, particle size, surface area, porosity, and reducibility of the catalysts. Consequently, these factors play a role in

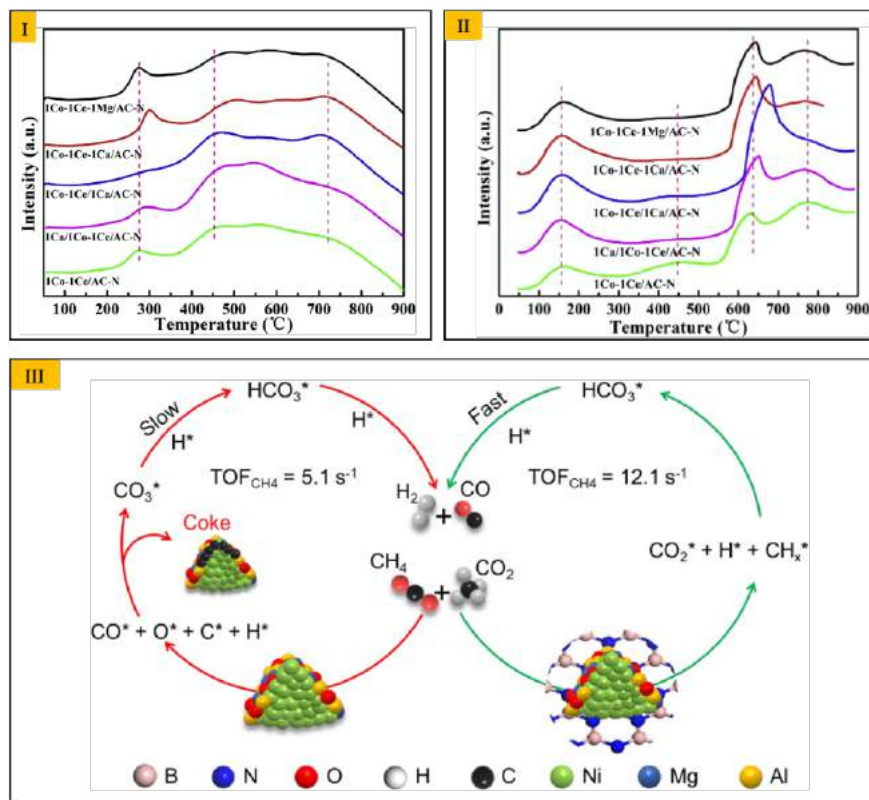


Figure 2.2: (I) H<sub>2</sub>-TPR patterns of calcined catalysts [1]; (II) CO<sub>2</sub>-TPD pattern of calcined catalysts [1]; (III) Possible reaction routes of the DRM reaction over modified catalyst [2].

determining the performance, stability, and selectivity of DRM catalysts. Furthermore, Takahashi et al. [127] tested the catalytic activity of the Ni/SiO<sub>2</sub>. The catalyst synthesized from depositing Ni in a sol-gel-derived wet silica gel has improved thermal stability, leading to greater dispersion of Ni phases on the support and thus making it inhibit carbon deposition during the DRM reaction. Through Ni/SBA-15 catalyst preparation by impregnation and co-precipitation, Albarazi et al. [129] established that the synthesis route has a remarkable effect on the physicochemical properties of the catalyst. However, the catalyst obtained from co-precipitation showed a smaller surface area compared to the unloaded SBA-15 support due to the presence of pore blockage, but the pore blockage was higher in the case of the catalyst prepared by the impregnation method. While for the case of impregnated catalysts, NiO particles with crystallite sizes around 9 to 11 nm were discovered outside the SBA-15 structure. This active phase dispersion has a remarkable effect on the final performance of a catalyst. Moreover, Dekkar et al. [130] compared the performance of two different catalysts synthesized using two distinct routes, namely microemulsion, and impregnation methods, towards DRM reaction. The results show that catalytic activities are significantly dependent on support properties, causing the synthesis method to heavily affect the catalyst properties. Finely dispersed Ni particles of less than 6 nm were observed on the catalyst synthesized by the microemulsion, also it also shows a high conversion of feed and stability of over 66 h. In addition to the large pore volume and HSA of the support, SMSI, which favors the homogeneous and finely dispersion of Ni metals on a support, is among the reasons behind the exceptional performance of this catalyst. However, it is not only the synthesis route that affects the performance of

the catalyst, but also the synthesis condition influences catalyst properties. Moreover, Damaskinos et al. [3] examined the impact of different  $\text{CeO}_2$  synthesis processes, including SG, Hydrothermal method (HT), Thermal decomposition method (TD), and Precipitation method (PT), on the carbon pathways during the DRM process as presented in Figure 2.3. According to four different preparation techniques, the 5 wt.% Ni supported on  $\text{CeO}_2$  carriers showed glaring structural and morphological variances, which resulted in significant variations in catalytic activity under the DRM reaction conditions. They observed that the maximum quantity of carbon deposition occurred after 12 h in the DRM, even though on Ni/ $\text{CeO}_2$ -HT less carbon was deposited during  $\text{CH}_4$  decomposition and more during CO disproportionation than on the other catalysts. This phenomenon is explained by the increased carbon deposition in the presence of both  $\text{CH}_4$  and CO, which has experimentally demonstrated to occur to a greater extent in Ni/ $\text{CeO}_2$ -HT.

## 2.3 DRM Reaction Mechanism

The DRM mechanism is summarized by Aramouni et al. [4] and Papadopoulou et al. [131] in four steps, as illustrated in Figure 2.4:

1.  $\text{CH}_4$  dissociative adsorption is a crucial step, with the dissociation energy influenced by surface properties. Generally, catalyst-dependent, this step is widely accepted as rate-determining. Partially dissociated  $\text{CH}_x$  species preferentially adsorb on sites completing their tetravalency,  $\text{CH}_3$  atop metal atoms and  $\text{CH}_2$  between two metal atoms (bridged adsorption). Step sites exhibit higher activity for  $\text{CH}_4$  adsorption and

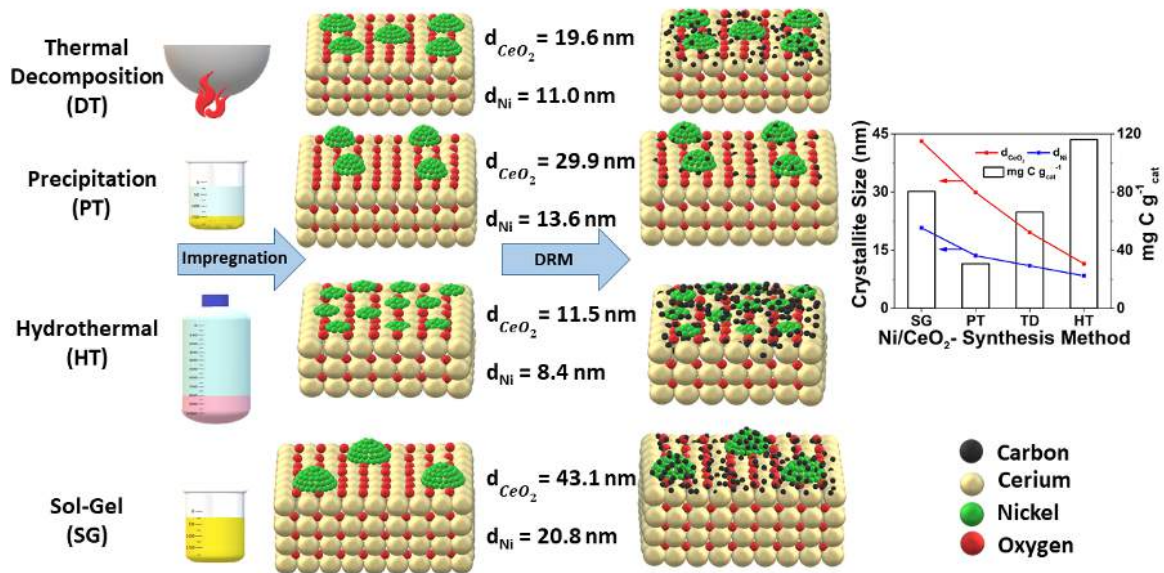


Figure 2.3: Different preparation methods of CeO<sub>2</sub> supported nickel catalysts for DRM reaction [3].

dissociation compared to close-packed surfaces.

2. CO<sub>2</sub> dissociative adsorption is influenced by surface structure and defects on several metals, occurring in three different coordination geometries: carbon coordination, carbon and oxygen coordination (carbon and one oxygen adsorbing, leaving one oxygen exposed), or oxygen coordination, where both oxygen atoms bond with the metal surface. The latter two geometries favor dry reforming and are generally rapid. The transfer of electrons to the CO<sub>2</sub> moiety is followed by an elongation of the C-O bond in relation to the free molecule.

3. Formation of hydroxyl groups: in dry reforming, the formation of hydroxyl groups has received less attention compared to steam reforming. Despite limited research on surface reaction mechanisms, it is established that the WGS reaction is at quasi-equilibrium, suggesting related surface reactions are fast. Developed models

indicate  $\text{H}_2$  migration from the active metal particle to the support, leading to the formation of hydroxyl groups at temperatures below 1073 K.

4. Surface reaction: the kinetic models predict hydrogen spillover from the metal surface to the support, leading to the formation of hydroxyl groups. Oxygen spillover from the support to the metal also occurs, with oxygen on the metal reacting with hydrogen-depleted  $\text{S1-CH}_x$  species to form either  $\text{S1-CH}_x\text{O}$  or  $\text{S1-CO}$  species during intermediates oxidation and desorption in dry reforming. The presence of hydroxyl groups on the support is unlikely at temperatures above 1,073 K as presented in Figure 2.4 [132]. Debate exists over whether  $\text{S-CH}_x\text{O}$  groups or adsorbed  $\text{CO}_2$ , forming carbonates, serve as precursors to CO, while some argue for direct formation of  $\text{S-CO}$  without an  $\text{S-CH}_x\text{O}$  intermediate. Consensus on the reaction mechanism details and the catalyst’s impact remains elusive, with catalyst nature and operating conditions playing crucial roles. Despite this uncertainty, many consider the formation/decomposition of formate  $\text{S-CH}_x\text{O}$  to CO and  $\text{H}_2$  as the rate-determining step, given the rapid desorption of CO and hydrogen, relative to SRM.

## 2.4 Catalysts Deactivation

A major obstacle in the development of novel, efficient catalysts for syngas production via DRM is long-term catalyst stability. Despite the choice of active metal and support structure, significant deactivation has been observed during DRM processes employing Ni and Ni-based catalysts. This frequently involves the oxidation of metal particles that are actively moving, sintering, and/or the deposition of carbon species produced

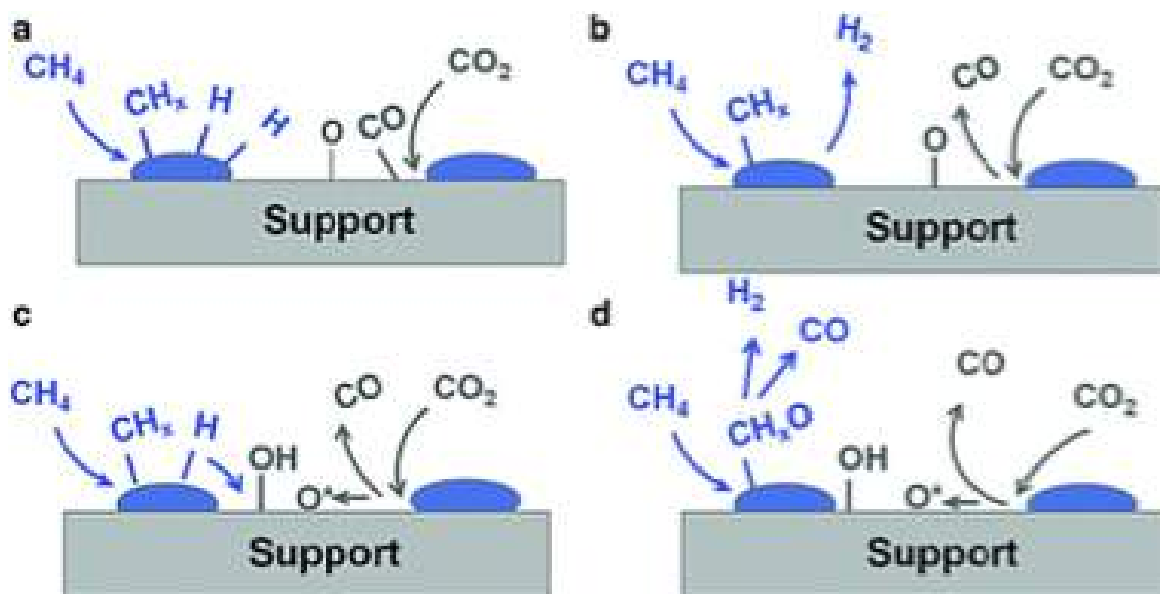


Figure 2.4: Illustration of DRM essential four steps [4].

from several chemical reactions such as RWGS,  $\text{CH}_4$  cracking, and Boudouard reaction. Although catalyst deactivation normally happens during DRM, its immediate and significant impacts can be reversed, delayed, or prevented [133][134]. These efforts were pursued with three main objectives: developing a highly stable catalyst, optimizing for slower catalyst deactivation, and gaining critical insights into the deactivation process. The growth of active crystallite size, carbon production, breakdown of support pore structure, and/or solid-state interactions between the active metal phase and the support or promoter are primary causes of catalyst deactivation in high-temperature DRM reactions [135].

### 2.4.1 Carbon/coke formation

Coke and carbon are produced in various ways, while Coke is produced by the condensation or breakdown of long-chain polymerized hydrocarbons on catalyst surfaces, and

| Rxn   | Reaction name                  | Reaction equation                                                                    | $\Delta H_{298}^\circ$<br>(kJ/mol) |
|-------|--------------------------------|--------------------------------------------------------------------------------------|------------------------------------|
| Eq.1  | RWGS                           | $\text{CO}_{2(g)} + \text{H}_{2(g)} = \text{CO}_{(g)} + \text{H}_2\text{O}_{(g)}$    | +41.12                             |
| Eq.2  | $\text{CH}_4$ cracking         | $\text{CH}_{4(g)} = \text{C}_{(s)} + 2\text{H}_{2(g)}$                               | +74.50                             |
| Eq.3  | Boudouard reaction             | $2\text{CO}_{(g)} = \text{C}_{(s)} + \text{CO}_{2(g)}$                               | -172.50                            |
| Eq.4  | Hydrogenation of $\text{CO}_2$ | $\text{CO}_{2(g)} + 2\text{H}_{2(g)} = \text{C}_{(s)} + 2\text{H}_2\text{O}_{(g)}$   | -90.22                             |
| Eq.5  | Hydrogenation of CO            | $\text{CO}_{(g)} + \text{H}_{2(g)} = \text{C}_{(s)} + \text{H}_2\text{O}_{(g)}$      | -131.34                            |
| Eq.6  | DRM                            | $\text{CH}_{4(g)} + \text{CO}_{2(g)} = 2\text{H}_{2(g)} + 2\text{CO}_{(g)}$          | +247.02                            |
| Eq.7  | Carbon gasification            | $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} = \text{CO}_{(g)} + \text{H}_{2(g)}$      | +131.0                             |
| Eq.8  | WGS                            | $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} = \text{CO}_{2(g)} + \text{H}_{2(g)}$    | -41.14                             |
| Eq.9  | $\text{CO}_2$ methanation      | $\text{CO}_{2(g)} + 4\text{H}_{2(g)} = \text{CH}_{4(g)} + 2\text{H}_2\text{O}_{(g)}$ | -164.75                            |
| Eq.10 | CO methanation                 | $\text{CO}_{(g)} + 3\text{H}_{2(g)} = \text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)}$   | -205.88                            |

Table 2.1: Possible gas phase reactions during the DRM reaction.

carbon is produced through the CO disproportionation reaction (Boudouard reaction) [136]. The evaluation of deactivation probability by carbon deposition from DRM and other reforming techniques is based on the stoichiometric O/C and/or H/C ratios in the feed [137]. The probability of carbon deposition increases with increasing the feed H/C and/or O/C ratio. Hence, in comparison to the other methods, DRM (H/C=2, O/C=1) is the most sensitive to carbon deposition. The amount and chemical composition of carbons and cokes produced during the DRM reaction are also strongly influenced by the nature of the feed, the kind of catalyst, and the reactor parameters [138].

Based on the findings of Wang et al. [139] the  $\text{CH}_4/\text{CO}_2$  ratio in the feed was found to strongly influence the chemical stability and morphology of the deposited carbon. TEM analysis of the spent Ni catalyst revealed that the encasing carbon, among the whisker, amorphous, and encasing carbon forms observed, was most likely responsible for the catalytic deactivation in the Ni/CaO-ZrO<sub>2</sub> catalyst, [135], supporting nature [140] and promoters [141][142] have been conventional to identify the carbon type pro-

duced and its impact on the catalytic deactivation. Three distinct processes result in the production and deposition of deactivating carbon on supported metal surfaces: (1) encapsulation of metal particles, which completely renders them in-active; (2) Monolayer chemisorption or physical adsorption in multilayers limits reactant gas access to active metal sites, while (3) continuous accumulation of active filamentous carbon in support material pores stresses and eventually fractures the support. This causes the catalyst pellets to deplete and the reactor space to become blocked [134]. Ni-based catalysts are favored for extensive industrial applications [143][144] but are sensitive to fast catalyst deactivation due to coke production, which can block and gradually reduce the active sites [145].  $\text{CH}_4$  cracking (Eq.2) and the Boudouard reaction are the main reactions by which carbon is formed (Eq.3). Different strategies have been employed to mitigate these drawbacks by altering the support type, incorporating promoters, and modifying the catalyst synthesis techniques [146]. Alloying Ni catalysts with metals such as Fe, Co, or Cu has emerged as one of the most promising approaches to enhance their catalytic performance [147]. Due to its affordability, Cu serves as an excellent choice for alloying metals. Ni-Cu alloys have gained significant attention in various chemical processes, particularly in the case of DRM, generating considerable interest [148][149]. It is widely accepted that the homogeneous composition of this alloy prevents the growth of Cu islands on the surface of Ni. Three bi-metallic catalysts were developed by Chatla et al. [150] to investigate the influence of varying Ni:Cu atomic ratios on metal sintering and prevention of coke deposition for DRM activity at 650 °C. At this temperature, coking and sintering reactions occur simultaneously; it was examined that the deactivation degrees were caused by sintering

and coke deposition on both the Ni-Cu and monometallic catalysts. The de-coking process can be initiated by introducing a  $\text{CO}_2$  stream, and the Mars-Van Krevelen mechanism can elucidate the coke removal process, especially when  $\text{CeO}_2$  support is employed Kong et al. [151]. By adsorbing and dissociating active carbon from  $\text{CO}_2$ , the  $\text{CeO}_2$  support replaces the OVs with the dissociated oxygen from  $\text{CO}_2$ . The carbon resulting from the dissociated  $\text{CH}_4$  then reacts with the active oxygen to generate CO. In a series of lanthanide oxide-promoted Ni/ $\text{Al}_2\text{O}_3$  catalysts, all the promoted materials exhibited superior carbon resistance compared to the unpromoted catalyst, leading to improved performance [152]. In this regard, the lanthanide oxides  $\text{CeO}_2$ ,  $\text{Nd}_2\text{O}_3$ , and  $\text{Gd}_2\text{O}_3$  promoted Ni/ $\text{SiO}_2$  [153], Ni/SBA-16 [154], Ni/MCM-41 [155] have improved their resistance to carbon, but there is still a lot of curiosity about how rare earth elements like La, Sm, Ce, and Gd act as catalysts for the oxidation of carbon species and MSI.

### 2.4.2 Metal sintering

Sintering, which is another form of catalyst deactivation caused by thermal effects, results in a decrease in the catalytic surface area. Additionally, sintering can lead to support pore collapse on active phase metals. This phenomenon occurs due to the decreased surface energy of the preferred crystallites and their size-dependent mobility on the support, which is kinetically favored [156]. Moisture, predominantly generated from RWGS reaction, is the primary cause of metal sintering, which commonly occurs at high temperatures during the DRM process, typically exceeding 700 °C. The primary mechanisms for active metal crystallite formation during high-temperature

DRM are atomic migration through coarsening and Ostwald ripening, and crystallite migration via coalescence [157]. Metal atoms are released from the crystallite during atomic migration and move over the support surface before being eventually trapped by larger crystallites. Agglomeration brought on by the migration of crystallites entails the movement of the entire crystallite across the support surface by collision and coalescence. In terms of application, it is impossible to rule out the idea that both mechanisms could operate simultaneously due to a variety of complex physico-chemical processes. These processes involve: releasing metal atoms from crystallites; adsorbing and trapping metal atoms on catalyst support pores and external surfaces; diffusing trapped atoms across support pores and surfaces; wetting support pores and surfaces with metal particles; nucleating metal particles; coalescing metal particles; and capturing metal atoms by larger metal particles [158]. Metal sintering moves slowly, especially at low reaction temperatures, yet they are typically challenging to prevent. Because of this, sintering prevention is simpler than sintering restoration. Encapsulation is the most efficient method of enhancing the stability of the catalysts. By using various synthesis techniques, Xu et al. [159] created a variety of encapsulated Ni catalysts (by silicalite-1 zeolite), and thorough characterization revealed that their structural properties—such as the degree of encapsulation—varied significantly, which affected their catalytic performance in DRM. The intrinsic properties of catalysts, prepared using various techniques, were crucial in preventing coking and Ni metal sintering during DRM. Fully encapsulated Ni within the support, with small particle sizes and SMSI in the Ni@SiO<sub>2</sub>-S1 catalyst, effectively inhibited coke formation during DRM.

## 2.5 Coke Resistance

The investigation of coke-resistant Ni catalysts is crucial considering the potential future large-scale applications of DRM [160][115]. Several methods have been explored to reduce coke formation [161]. Firstly, metal oxides like  $K_2O$ ,  $MgO$ , or  $CaO$  have been used as basic supports or promoters to enhance the dissociative adsorption or activation of  $CO_2$  [162]. Additionally,  $CeO_2$  and  $ZrO_2$ , with their high oxygen mobility facilitating coke oxidation, have been extensively studied [163]. Secondly, precious metals such as Pt, Rh, Ru, Pd, and Ir have been employed to provide active sites with higher resistance to coke formation [164]. These precious metals have also been used as promoters alongside Ni catalysts to improve NiO dispersion and reducibility or alter the carbon formation pathway to reduce coke deposition [165]. However, their use is impractical due to cost considerations; as a result, alloying Ni with cheaper metals such as Co, Ba, Cu, Mn, Sn, Mo, and Fe has been attempted [166]. Alloying can reduce the domain size of Ni ensembles responsible for coke generation or impede the diffusion of carbon through the metallic particle lattices [167]. Nevertheless, alloying often leads to decreased activity due to a lower number of catalytically active sites, and long-term stability is typically poor [168]. Thirdly, the preparation of smaller-sized Ni NPs has been achieved through the exploitation of SMSI. Smaller Ni NPs have fewer Ni terraces, which impede coke deposition. SMSI induce the formation of smaller Ni NPs during synthesis and prevent their aggregation to some extent during the reaction. Improved Ni dispersion and smaller particle sizes have also been achieved through plasma treatment [169], microwave irradiation [170] and the reduction of

Ni-containing perovskites [171]. However, the high reaction temperatures involved in DRM, such as 800 °C, eventually lead to the aggregation of small Ni NPs over time, resulting in increased coke deposition and degraded activity. Han et al. [172] developed coke-resistant Ni catalysts by immobilizing pre-produced Ni NPs (5.2 nm) onto functionalized SiO<sub>2</sub> supports and coating them with SiO<sub>2</sub> overlayers. These catalysts showed stable operation for 170 h without activity degradation, unlike Ni catalysts without SiO<sub>2</sub> coating, which experienced severe sintering and carbon filament formation during DRM. The coke-resistant Ni catalyst holds the potential for various hydrocarbon transformations. However, the risk of coke formation on Ni catalysts during DRM is significantly higher, especially as a high CO<sub>2</sub>/CH<sub>4</sub> feed ratio cannot be used to inhibit coke formation. The deactivation of catalysts due to coke formation is particularly severe in DRM. Certain carbon forms can diminish catalyst activity, while others do not. For example, amorphous carbon and graphite platelet films can envelop the catalyst's metal surface. At elevated temperatures, atomic carbon can penetrate the Ni surface layers to a depth of 50-70 nm. The accumulation of adsorbed carbon, whether at high or low temperatures, can deactivate the active sites of the metal[173].

According to Trimm [174], the dissolution of carbon in Ni plays a crucial role in the growth of carbon whiskers, starting with the formation of nickel carbide [175]. This understanding can serve as a foundation for the development of coke-resistant Ni catalysts. Numerous experimental and theoretical studies have confirmed the significant impact of Ni particle size on coke formation [176]. Restricting the size of the Ni catalyst can enhance its resistance to coke deposition. This can be achieved

through the use of promoters, changes in the support material, or adjustments in catalyst preparation techniques. However, it is important to note that the size-dependent properties of Ni catalysts are not governed by simplistic models. The effects of morphology, structure, and composition are equally important. Therefore, the design and controlled preparation of Ni-based catalysts must consider the synergy between size, morphology, structure, and composition. Well-defined supporting materials, such as metal oxides or molecular sieves, can serve as sources of small Ni particles. Additionally, catalysts or supports with basic properties facilitate the reaction between  $\text{CO}_2$  and carbon, thereby increasing the catalyst's resistance to coke formation [177]. The use of redox promoters in the catalyst formulation can also enhance coke resistance [174]. Furthermore, an SMSI can significantly improve coke resistance. The concept of SMSI can also mitigate Ni sintering. These various factors provide opportunities for the improvement of catalyst design and preparation.

## CHAPTER 3

# METHODOLOGY

### 3.1 Materials

Hexadecyltrimethylammonium bromide, [CTAB ((CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N(Br)(CH<sub>3</sub>)<sub>3</sub>; 99%)], lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), Silica (SiO<sub>2</sub>), and zinc oxide (ZnO) were purchased from Sigma-Aldrich. Toluene was purchased from Honeywell [(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>; 99.9%)], tetraethyl orthosilicate, [TEOS (SiC<sub>8</sub>H<sub>20</sub>O<sub>4</sub>; 99%)], urea (CH<sub>4</sub>N<sub>2</sub>O), and n-butanol (C<sub>4</sub>H<sub>10</sub>O; 99%) were obtained from Merck. Nickel (II) acetate tetrahydrate (Ni(OCOCH<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O; 99%) was purchased from Fluka Chemika. Deionized water (DI) was employed in all synthesis procedures, and the reactant gases CH<sub>4</sub>/CO<sub>2</sub> (50/50) were obtained from Air Products. The chemicals utilized were all of analytical quality and were not modified in any way.

## 3.2 Catalyst Synthesis

### 3.2.1 Ni-based Fibrous Silica Zinc-oxide (NSZF) Catalysts

The microemulsion method was employed to produce the SZF support, utilizing CTAB as the surfactant, urea as the hydrolyzing agent, toluene as the oil phase, and butanol as the co-surfactant to aid in the formation and stabilization of micelles. Typically, a solution was prepared by dissolving 5.82 g of CTAB and 3.48 g of urea in 173 mL of DI water. Then, the solution was stirred for 15 min at 25 °C, and 8.5 mL of butanol and 173.9 mL of toluene were added. Subsequently, 1.6 g of ZnO was added while the solution was stirred for 30 min. Next, 12.7 mL of TEOS was added drop by drop while stirring for 10 min. The solution was stirred for 6 h before being placed in an oven at 120 °C for 8 h. Afterwards, the solution was washed and centrifuged at 4000 rpm before being dried at 120 °C for 12 h. The obtained product was then calcined at 550 °C in the atmosphere for 6 h, resulting in the collection of the SZF support. The wet impregnation approach was utilized to load Ni on the SZF support. Initially, the nickel acetate tetrahydrate was dissolved in DI water, followed by adding the SZF support. The solution was stirred at 80 °C for 8 h and then dried overnight. The resulting material was then calcined for 3 h at 700 °C to produce the NSZF-x catalysts.

### 3.2.2 Ni-based Fibrous Silica Lanthanum-oxide (NSLF) Catalysts

Typically, the hydrolyzing agent ( $\text{CH}_4\text{N}_2\text{O}$ ), the co-surfactant ( $\text{C}_4\text{H}_{10}\text{O}$ ), the surfactant (CTAB), and the oil phase ( $\text{C}_6\text{H}_5\text{CH}_3$ ) were utilized in the synthesis procedures to aid in micelle formation and stability, with  $\text{La}_2\text{O}_3$  serving as the core for the development of SLF, as illustrated in Figure 3.1. Firstly, a solution was prepared by mixing 3.48 g of  $\text{CH}_4\text{N}_2\text{O}$  and 5.82 g of CTAB in 173 mL of DI water. Then, 173.9 mL of  $\text{C}_6\text{H}_5\text{CH}_3$  and 8.5 mL of  $\text{C}_4\text{H}_{10}\text{O}$  was added to the solution, and stirred for 30 min at 25 °C. Subsequently, 1.65 g of  $\text{La}_2\text{O}_3$  was introduced, and the solution was stirred for 15 min. Afterwards, 12.7 mL of  $\text{SiC}_8\text{H}_{20}\text{O}_4$  was added dropwise while stirring. Following 6 h stirring, the solution was maintained at 120 °C inside the oven for 8 h. The obtained solution was rinsed with ethanol and water and then centrifuged at 7000 rpm. The product was dried at 120 °C for 12 h and calcined in the atmosphere for 6 h at 550 °C to obtain the SLF support. Then, the wet impregnation was used to load various amounts of Ni to the developed SLF. A calculated quantity of  $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ , employed as a metal precursor, was typically dissolved in DI water before being added to SLF and continuously stirred at 80 °C until it formed a slurry. The composite was dried overnight at 80 °C, then crushed to a powder, and calcined for 3 h at 700 °C to decompose the precursor source.

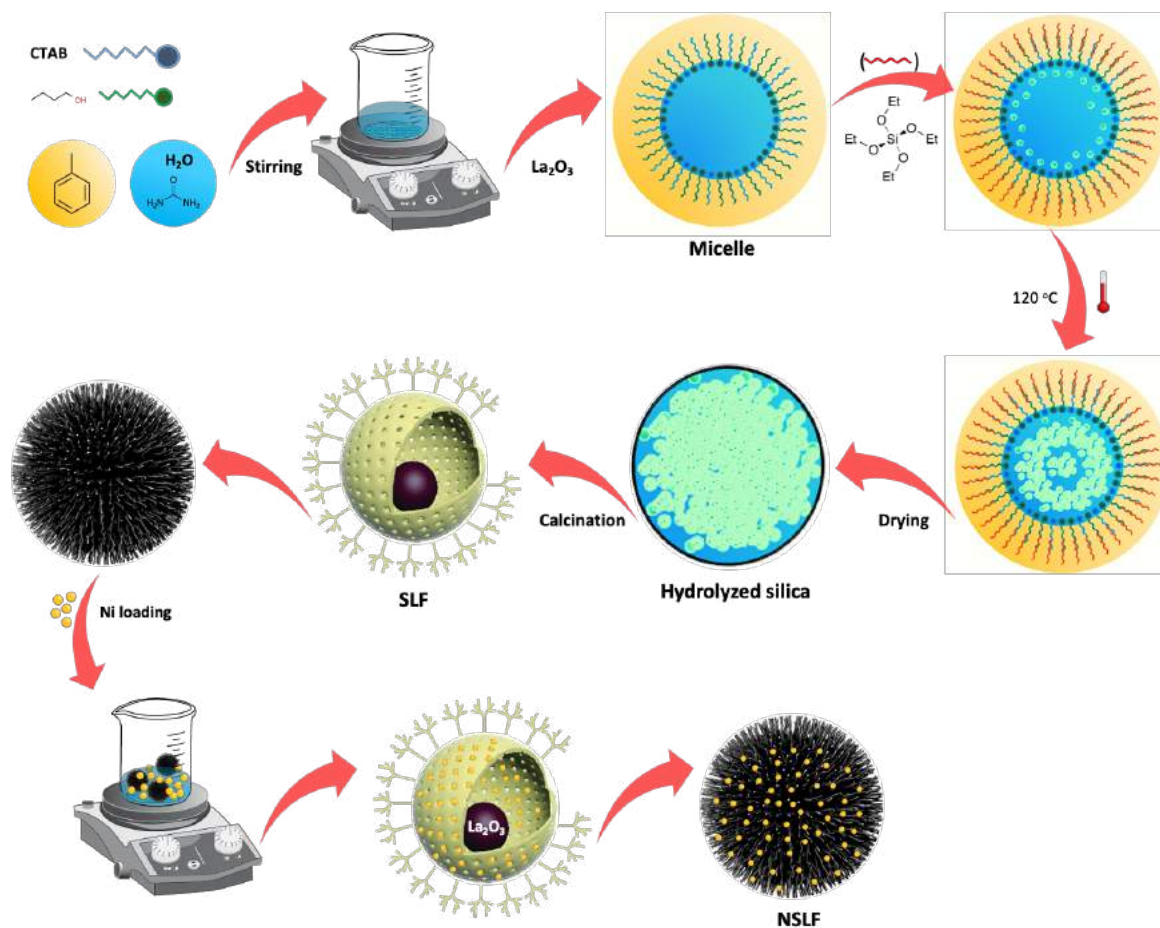


Figure 3.1: A schematic diagram of the synthesis of NSLF catalysts.

### 3.2.3 Ni-based Silica Lanthanum-oxide (NSL-C) Catalyst

The composite of  $\text{SiO}_2$ - $\text{La}_2\text{O}_3$  was synthesized using the incipient-wetness impregnation method with commercial  $\text{SiO}_2$  and  $\text{La}_2\text{O}_3$ . The calculated amounts of  $\text{La}_2\text{O}_3$  and  $\text{SiO}_2$  were gently mixed and stirred in the presence of DI water for 10 h, then dried overnight at  $80^\circ\text{C}$  in a drying oven. Subsequently, the obtained powder was calcined in air at  $600^\circ\text{C}$  for 5 h. The resulting  $\text{SiO}_2$ - $\text{La}_2\text{O}_3$  was loaded with 10 wt.% Ni using the wet impregnation method.

## 3.3 Characterizations

Various characterization techniques were used to study the catalysts' characteristics.

The phase identification and crystallinity of the catalysts were determined using an X-ray diffraction (XRD). Two instruments, a Bruker S8 TIGER WDXRF spectrometer and a Rigaku Ultima IV diffractometer, were employed for this purpose. The catalysts were scanned at a steady rate of  $5.0^\circ/\text{min}$  between  $20^\circ$  and  $80^\circ$ .

A Nicolet iS10 Fourier transformation infrared (FTIR) spectrometer was used to analyze the functional groups present in the catalysts. The pellet discs were prepared by mixing KBr with the catalyst at a ratio of 100:1 to prepare the samples for analysis. The pelletized sample was then analyzed by directing the IR source toward the samples and recording the spectra.

The surface morphology of the fresh catalysts was studied using Field Emission Scanning Electron Microscopy (FESEM) (Thermo Fisher Quattro S unit). The catalysts were crushed into a powder, sprinkled onto a sticky tape, and coated with a

thin layer of gold under a vacuum for 10 min. The scanning was carried out at 30 kV accelerating voltage, using Secondary electron (SE) and Backscattered electron (BSE) modes. Additionally, the FESEM unit was equipped with an EDX detector supplied by Oxford, Inc. to perform the elemental analysis.

TEM (JEOL JEM-2100F) was also used to examine the synthesized and spent catalysts. For the analysis, 0.05g of catalyst was dissolved in ethanol and ultrasonicated for 10 min to ensure a homogeneous dispersion. A 5  $\mu$ L droplet of the diluted solution was then carefully placed on a pure carbon grid with a mesh size of 300. The sample was air-dried for an additional hour in a pumping station to allow the solvent to evaporate completely.

A TriStar II Plus device was used to calculate the pore volume and BET surface area using  $N_2$  adsorption-desorption isotherms and the pore size and pore volume were calculated using the Barrett–Joyner–Halenda (BJH) technique. The catalysts were degassed for 3 h at 300  $^{\circ}$ C for 3 h before conducting the measurements.

The catalysts were examined using XPS to examine their composition and chemical state via a PHI 5000 Versa Probe II spectroscope (ULVAC-PHI Inc.) unit. The catalysts had been prepared as pelletized discs and exposed to high vacuum conditions before evaluation.

The catalytic reducibility was investigated using hydrogen temperature-programmed reduction ( $H_2$ -TPR; the BELCAT-A-200 unit) analysis. The  $H_2$  consumption was recorded using a Thermal conductivity detector (TCD) while introducing helium (He) into the background flow. The redox properties were evaluated using an Ar/ $H_2$  (90/10 vol%) at a flow rate of 50 mL/min. The catalyst underwent 3 h pre-

treatment in high-purity helium at 300 °C. It was then cooled to room temperature and heated to 800 °C at a rate of 20 °C/min under H<sub>2</sub>.

The BELCAT II equipment was utilized to conduct a CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) analysis to study the catalysts' basicity. The sample underwent pre-reduction using an H<sub>2</sub>/Ar (10/90 vol%) mixture at a flow rate of 50 mL/min for 3 at 300 °C. Subsequently, CO<sub>2</sub> was introduced by cooling the device, and the temperature was gradually increased to 120 °C while helium was introduced to sweep away any remaining CO<sub>2</sub>. The TCD signal was continuously recorded as the temperature was raised to 800 °C at a rate of 20 °C/min.

The carbonaceous species of the spent catalysts were examined using a HORIBA Scientific LabRAM HR Raman spectroscopy unit equipped with an internal He-Ne 17 mW red laser at 633 nm, with the laser power set to 25%, four times accumulation, and an acquisition duration of 20 s.

Additionally, Scanning electron microscopy (SEM) (JSM-6610LV) was employed to analyze the spent catalysts. For this analysis, the material was crushed into small pieces, coated with gold under a vacuum of 50 Pa for 10 min, and then sprinkled onto double-sided sticky tape.

The carbon deposition on the spent catalysts was examined by Thermogravimetric analysis (TGA) (SDT Q600) over a temperature range of 30-800 °C.

### 3.4 Catalyst Performance

The DRM reaction was performed under atmospheric pressure in a fixed-bed tube reactor, which was heated using a furnace with a programmable temperature controller, as shown in Figure 3.2. Basically, 0.2 g of the catalysts (300-500 nm particle sizes) were loaded onto quartz wool for support and placed at the center of the tube reactor. The tested catalyst underwent a 2h reduction at 700 °C under a flow of H<sub>2</sub>/Ar (10/90) before the reaction. Subsequently, the reactor reached the desired reaction temperature, and a mixture of CO<sub>2</sub>/CH<sub>4</sub> (50/50) reactant was introduced into the reaction system. The reactor was then set up to gradually rise in temperature from 500 to 1000°C with 50°C intervals to evaluate the catalytic activity. Furthermore, the catalytic stability was examined by keeping the catalyst under the stream at a GHSV of 12,000mL/g<sub>cat</sub>.h at 750 °C. An online gas chromatograph (6890 N Agilent GC) equipped with a TCD detector was used to monitor the gases of the reactants and the products. Then, the results were collected and expressed by using the following calculations to obtain conversion, product selectivity and yield, and syngas ratio:

$$CH_4Conversion = \frac{F_{(CH_4)in} - F_{(CH_4)out}}{F_{(CH_4)in}} \times 100 \quad (3.1)$$

$$CO_2Conversion = \frac{F_{(CO_2)in} - F_{(CO_2)out}}{F_{(CO_2)in}} \times 100 \quad (3.2)$$

$$H_2Yield = \frac{F_{(H_2)out}}{2F_{(CH_4)in}} \times 100 \quad (3.3)$$

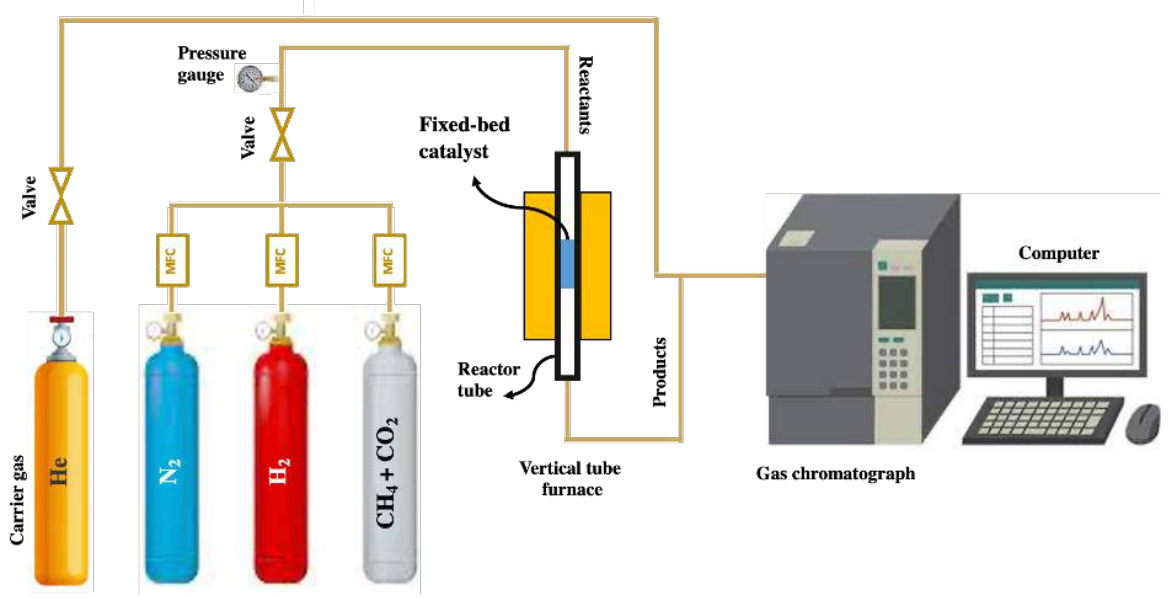


Figure 3.2: Schematic diagram of the reactor setup for DRM process.

$$COYield = \frac{F_{(CO)out}}{F_{(CH_4)in} + F_{(CO_2)in}} \times 100 \quad (3.4)$$

$$H_2Selectivity = \frac{F_{(H_2)out}}{2[F_{(CH_4)in} - F_{(CH_4)out}]} \times 100 \quad (3.5)$$

$$COSelectivity = \frac{F_{(CO)out}}{[F_{(CH_4)in} - F_{(CH_4)out}] + [F_{(CO_2)in} - F_{(CO_2)out}]} \times 100 \quad (3.6)$$

$$\frac{H_2}{CO} = \frac{F_{(H_2)out}}{F_{(CO)out}} \times 100 \quad (3.7)$$

Where  $F_{out}$  represents the outlet flow rate, while  $F_{in}$  represents the inlet flow rate.

## CHAPTER 4

# RESULTS AND DISCUSSIONS

### 4.1 Ni-based Fibrous Silica Zinc-Oxide (NSZF)

#### Catalysts

Herein, our objective was to investigate the impact of incorporating ZnO into the fibrous silica framework as both a core and a co-support. Our aim was to enhance H<sub>2</sub> selectivity, reduce CO selectivity, minimize activity loss, and improve stability during the DRM reaction. Additionally, we explored the influence of ZnO on the physicochemical properties of the fibrous silica framework and assessed the role of morphological structure in this context, evaluating the potential of the co-supported catalyst (SZF) for DRM. Furthermore, SZF-based nickel catalysts were synthesized with varying nickel loadings and optimized as active catalysts for DRM to evaluate the effect of nickel loading amounts (3-20 wt.%) on catalytic performance. We hypothesized that the addition of Ni into SZF could initiate a synergistic effect, resulting in enhanced dispersion of the active component and strengthened MSI. This

enhancement can boost catalytic activity and yield higher syngas in DRM reaction.

#### 4.1.1 Fresh catalysts characterization

Figure 4.1a displays the results of XRD patterns conducted on the prepared catalysts to determine their crystallinity and phase states. The diffraction peaks observed at  $37.0^\circ$ ,  $43.1^\circ$ , and  $62.8^\circ$  were recognized to the presence of NiO (COD card No. 00-432-0508). NiO diffraction peaks showed a gradual increase in intensity from 3 wt.% to 20 wt.% when Ni loading quantities were increased, suggesting that the loading amounts had an impact on Ni dispersion across the SZF support. The diffracted peaks at  $31.7^\circ$ ,  $34.43^\circ$ ,  $36.2^\circ$ ,  $47.5^\circ$ ,  $56.6^\circ$ ,  $62.9^\circ$ ,  $66.39^\circ$ , and  $67.9^\circ$  were recognized to the ZnO and well matched with COD card No. 00-230-0450. Also, the  $\text{SiO}_2$  was observed at  $2\theta$  value of  $22.0^\circ$ ,  $24.3^\circ$ ,  $25.2^\circ$ , and  $44.9^\circ$  according to COD card No. 00-412-4082. Notably, NSZF-3 catalyst exhibited reduced NiO peak intensities than the other catalysts. This shows that NiO species were more evenly distributed on SZF support. Because of the varied accessibilities, the shape of the mesoporous channels with high surface areas and pore volumes influenced the dispersion of NiO species significantly. However, this limited the availability of the Ni during the impregnation. Overall, the dispersion of Ni observed in NSZF catalysts was attributed to the presence of fibrous shell structure, which uniformly extended from the free radical directions and the center of the SZF framework. This facilitated straightforward access to the Ni precursor. Consequently, SZF with fibrous mesoporous channels demonstrates promise as a support option for the design of sintering-resistant catalysts with high metal loading capacities. Additionally, the strength of the NiO diffraction peak in

NSZF catalysts increased with higher loading amounts. According to the Scherer equation (Table 4.1), the size of the Ni particles within the catalyst expanded from 8.6 nm to 16.7 nm, which indicates that the dispersion of the Ni metal was influenced by the quantity of its loading.

The structural characteristics and functional groups of the catalysts were examined using FTIR spectroscopy in the wavenumber range of 4000–400  $\text{cm}^{-1}$ , as shown in Figure 4.1b. In the 1400–400  $\text{cm}^{-1}$  region, prominent peaks indicated the presence of siliceous frameworks characterized by various Si-related bonds, including Si-O, Si-OH, Si-O-Zn, Si-O-Si, and Zn-O bonds [178]. Analysis of the spectra revealed distinct bands at 1225, 1101, 943, 806, and 467  $\text{cm}^{-1}$  for all samples, indicating the development of the silica structure primarily because of the stretching of Si-O-Si bonds. The wide humps observed in all samples represented adsorption bands centered at 1225  $\text{cm}^{-1}$  and 1101  $\text{cm}^{-1}$ , confirming the presence of the siliceous framework [179][180]. The small bands found at 943 and 1632.8  $\text{cm}^{-1}$  indicated the presence of external Si-OH groups [181]. Also, the stretch vibrations of symmetric and asymmetric bands of Si-O-Si were detected at 806  $\text{cm}^{-1}$  and 1101  $\text{cm}^{-1}$ , respectively [182]. A peak at 467  $\text{cm}^{-1}$  indicated the bending vibration of X-O-X, while a band around 1225  $\text{cm}^{-1}$  suggested the presence of the stretches of X-O symmetric, where X is either Si or Zn [183]. The incorporation of Ni ions resulted in the formation of Si-O-Ni, leading to a decrease in intensities at 943  $\text{cm}^{-1}$  and 1101  $\text{cm}^{-1}$ , which was observed in the SZF without the Si-O-Ni bond. The observed intensities varied with the Ni loading on the SZF support, with significant shifts noted at 1225  $\text{cm}^{-1}$  due to the scattering of NiO on the SZF surface and the reduction in core aspects of the siliceous framework.

This incorporation of Ni also led to the degradation of the silica catalyst structure by substituting Si-O-Si and Zn-O bonds. With the addition of 15 wt.% Ni onto SZF, there was a significant reduction in the intensity of the stretching vibration mode of Si-O-Si at  $1101\text{ cm}^{-1}$ , illustrating strong incorporation of Ni onto SZF and the formation of Si-O-Ni and Zn-O-Ni bonds, replacing the original Si-O-Si and Zn-O-Si bonds, respectively. Furthermore, an additional peak around  $3445\text{ cm}^{-1}$  indicated interactions among the OH hydroxyl groups,  $\text{H}_2\text{O}$ , and Si-OH [184].

Figure 4.1(c,d) presents  $\text{N}_2$  adsorption-desorption isotherms and the pore size distribution of NSZF catalysts. The results demonstrate the excellent thermal stability of the prepared catalysts, as indicated by the maintaining type IV isotherm and H4 hysteresis loops after loading [185]. This highlights the resilience of the SZF support, which exhibited remarkable characteristics such as the highest BET surface area of  $147.8\text{ m}^2/\text{g}$  and a pore volume of  $0.37\text{ cm}^3/\text{g}$ , as shown in Table 4.1. However, introducing the active metal (Ni) resulted in a significant decrease in pore volume and surface area across all carriers, recognized as the active metal occupying space within the carrier channels and blocking the pores during the impregnation process [186]. Nonetheless, the unique pore structure of SZF proved advantageous for accommodating high concentrations of active components. While the pore size of NSZF-3, NSZF-5, NSZF-10, and NSZF-20 catalysts marginally diminished, signifying the effective integration of NiO particles into the carrier pores, there were no notable changes in the isotherm as the Ni loading from 3% to 20%. This suggests that elevated loadings did not affect the structural stability of the support [187]. The NSZF catalysts displayed predominant pore sizes around 11 nm, indicating excellent dispersibility

even in the heavily loaded NSZF-15 catalyst. However, there was a slight increase in pore size observed in the NSZF-10 and NSZF-20 catalysts, and the reduction in pore volume and surface area became more pronounced with higher Ni loadings, indicating increased occupation of the carrier pores by Ni particles [188]. The NiO crystallite diameters developed from 8.64 to 16.7 nm when Ni loadings increased from 3 to 20 wt.%. However, with 20 wt.% Ni loading, there was a considerable increase in NiO crystallite size (16.7 nm), indicating that active metals agglomerated on the support's external surface due to difficulties with integrating them into the porous framework. Larger Ni nanocrystalline sizes are reported to be prone to coke deposition, resulting in rapid catalytic deactivation and limited access to active sites for gas reactants [189].

| Catalysts | Ni content (%) <sup>a</sup> | Surface area (m <sup>2</sup> /g) <sup>b</sup> | Total pore volume (cm <sup>3</sup> /g) | Pore size (nm) | Ni crystallite size (nm) <sup>c</sup> |
|-----------|-----------------------------|-----------------------------------------------|----------------------------------------|----------------|---------------------------------------|
| SZF       | -                           | 147.8                                         | 0.367                                  | 9.96           | -                                     |
| NSZF-3    | -                           | 112.8                                         | 0.315                                  | 11.2           | 8.64                                  |
| NSZF-5    | 6.9                         | 122.5                                         | 0.339                                  | 11.1           | 9.37                                  |
| NSZF-10   | 11.1                        | 120.7                                         | 0.319                                  | 19.12          | 14.27                                 |
| NSZF-15   | 16.8                        | 139.9                                         | 0.340                                  | 11.17          | 14.27                                 |
| NSZF-20   | 19.5                        | 119.7                                         | 0.282                                  | 14.76          | 16.7                                  |

<sup>a</sup> Determine from the XRF

<sup>b</sup> Determine from the BET and BJH

<sup>c</sup> Determine from the Scherrer equation

Table 4.1: Textural properties of the synthesized NSZF catalysts.

The morphology of the designed catalytic systems is illustrated in Figure 4.2 through FESEM micrographs and elemental mapping, providing valuable insights into the distribution of NiO crystallites on the support. Figure 4.2(a,b) depicts the spherical shapes of the fibrous shell structure of silica in the SZF support. In all loaded catalysts, NiO particles were observed as bright yellow spots dispersed on the

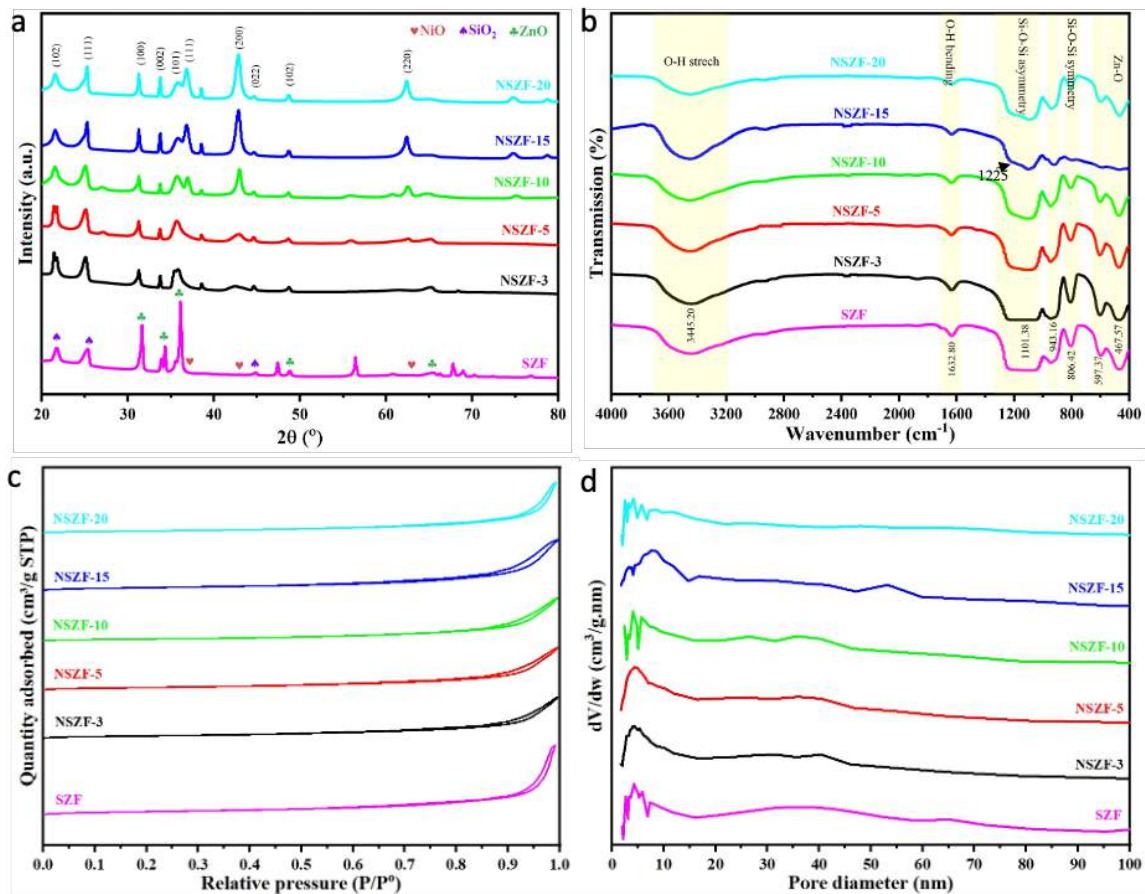


Figure 4.1: (a) XRD patterns, (b) FTIR patterns, (c) N<sub>2</sub> adsorption-desorption isotherms, and (d) pore size distribution of NSZF catalysts.

SZF structure, as obtained by EDX mapping. Remarkably, even after loading with Ni using the wet impregnation method, the fibrous silica shell structure remained intact. However, a slight distortion in the sphericity of the SZF was noted due to the loading of Ni, as presented in Figure 4.2(d-h). The analysis revealed a well-dispersed and monodisperse distribution of NiO particles, demonstrating a narrow particle size distribution and an absence of visible particle agglomeration. The existence of several accessible active sites is indicated by the highly dispersed Ni species on the SZF surface. The Ni particles were well-dispersed in the NSZF-15, according to a summary of the particle sizes derived from the XRD data reported in Table 4.1 via the Scherrer equation. This indicates that the 15 wt.% Ni loading resulted in a more even and homogeneous distribution of Ni on the SZF, highlighting the superiority of this particular loading concentration. However, increasing the Ni loading in the NSZF-20 catalyst did not significantly impact the metal distribution. In the NSZF-20 catalyst, massive NiO aggregates were randomly scattered across the surface, suggesting that the additional Ni did not contribute to a more uniform distribution. Notably, the NiO NPs in NSZF-20 catalyst exhibited a considerably larger size among the catalysts. This can be associated with the accumulation of crystallized metals caused by excessive Ni loading, which results in the development of larger particles. However, achieving a homogeneous dispersion of NiO particles with a smaller diameter offers advantages in preventing coking, according to the literature [190][191]. This inhibits the migration of Carbon nanotubes (CNTs) toward the catalytic interface, increasing reactivity between CNTs and the surface oxygen lattice and minimizing carbon formation [192].

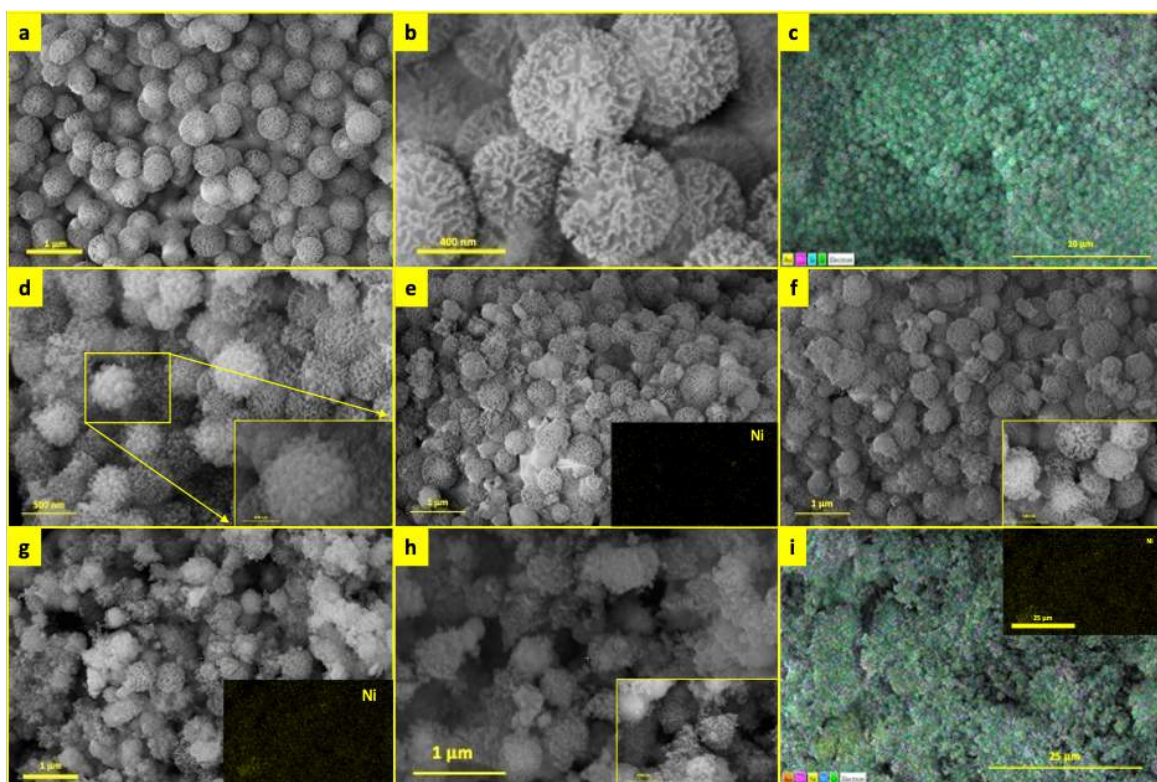


Figure 4.2: FESEM-EDX images of the catalysts; (a,b) SZF support, (c) SZF support mapping, (d) NSZF-3, (e) NSZF-5, (f) NSZF-10, (g) NSZF-15, (h) NSZF-20, and (i) NSZF-20 mapping.

TEM micrographs of the SZF support reveal the presence of well-ordered microspheres surrounded by a fibrous shell structure in all axial directions, as depicted in Figure 4.3(a-c). Figure 4.3(d-i) shows the TEM images and the corresponding NiO particle sizes of NSZF catalysts. The Ni addition to SZF maintained the original spherical structure of SZF, with fibers completely loaded and extending outward. For different Ni loadings on SZF, ranging from 7 to 14 nm (centered at 10 nm), different distributions and sizes of NiO NPs were observed. These NPs were indicated by dark and contrasting spots, visible only in certain areas. In contrast, the NSZF-15 catalyst exhibited a high distribution of Ni compared to the other loadings, indicating the superiority of the 15 wt.% Ni loading. This is further supported by Figure 4.3, which demonstrates that increasing the loading to 20 wt.% did not yield a positive effect on the Ni dispersion. On NSZF-20, large NiO deposits were lightly distributed. The NiO NPs in the higher loading were notably larger and accumulated compared to those in the other catalysts. This increase in size can be associated with the agglomeration of crystals from the high Ni loading. Consistent with the earlier postulation based on the XRD and FTIR results, the optimal 15 wt.% Ni loading exhibited highly homogeneous dispersion of NiO. This dispersion may be attributed to the presence of a SMSI in NSZF-15. Additionally, the unique hierarchical pore structure of SZF provided ample interparticle pores, which accommodated the optimal Ni loading. The uniform distribution of smaller NiO particle sizes in NSZF-15 offered advantages in terms of minimizing coke formation in which directed CNTs to the catalyst contact, boosting their interaction with the oxygen lattice.

Additionally, XPS was utilized to investigate the oxidation state and chemical

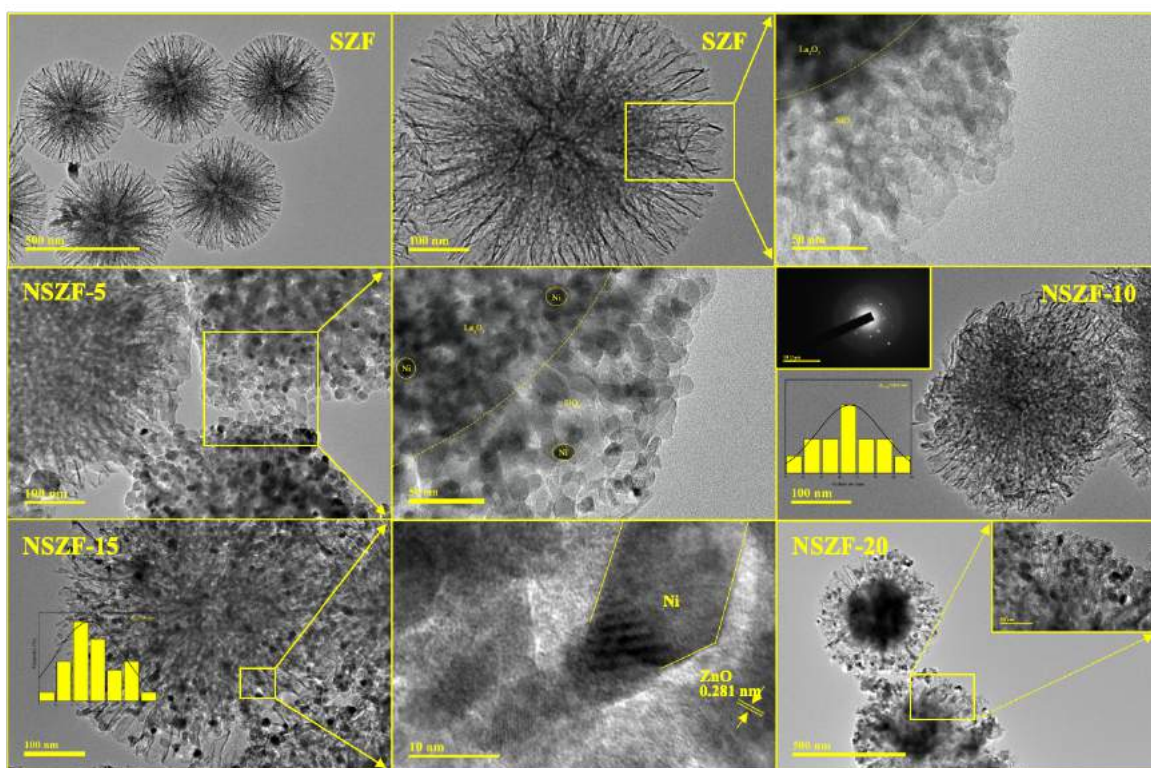


Figure 4.3: TEM images of the prepared NSZF catalysts; (a-c) SZF, (d,e) NSZF-5, (f,g) NSZF-10, and (h,i) NSZF-15 catalysts.

environment of the surface of NSZF-5, NSZF-10, and NSZF-15 catalysts, aiming to identify the presence of nickel species. Figure 4.4 displays the spectra of Ni 2p, revealing a deconvolution into two peaks attributed to the presence of Ni 2p<sub>1/2</sub> and Ni 2p<sub>3/2</sub> because of the interaction of spin-orbit [193]. The major peak for Ni<sup>2+</sup> ions and its satellite peak are detected in the Binding energy (BE) of 855.7-856.1 eV and 861.8-862.5 eV, respectively. Similarly, a peak of Ni<sup>2+</sup> 2P<sub>3/2</sub> is observed. The literature has demonstrated that Ni particles located outside the pores are more prone to oxidation from the surrounding environment compared to Ni particles that have infiltrated into the pores. Moreover, the BE of Ni 2p<sub>3/2</sub> in NiO is typically around 854 eV [194]. The spectra reduction and partial Ni<sup>2+</sup> incorporated within the SZF led to the growth of the peaks at 873 eV and 853 eV as Ni<sup>0</sup> species. Furthermore, a considerable interaction with SZF was observed as the source of the satellite peaks at 862 eV and 880 eV, as well as the peaks observed at 874 eV and 856 eV, were recognized as the Ni<sup>2+</sup> species [195]. Additionally, Figure 4.4 b illustrates the presence of two major peaks related to Zn 2p<sub>1/2</sub> (1046.23 eV) and Zn 2p<sub>3/2</sub> (1023.03 eV) in the NSZF-5, NSZF-10, and NSZF-15 catalysts. These peaks provide confirmation of the Zn atom's presence within the lattice of the ZnO crystal. ZnO is distinguished by 23.2 eV BE variance between the Zn 2p<sub>1/2</sub> and Zn 2p<sub>3/2</sub> peaks [196]. Moreover, in Figure 4.4 c, the XPS pattern exhibits a characteristic peak at 103.5 eV, which corresponds to Si-O in SiO<sub>2</sub>. This observation provides evidence that SiO<sub>2</sub> has successfully formed and grown on the surface as a fibrous shell [197]. Furthermore, the catalyst surface's oxygen vacancies (O<sub>V</sub>) greatly improve CO<sub>2</sub> activation and adsorption, which aid in the formation of CO and O\* species [198]. This mechanism is critical to increasing the activity of

the DRM process. In this work, we used O 1s XPS spectra to determine the amounts of  $O_V$  in the catalysts that were synthesized. Figure 4.4 d depicts the O 1s spectra of all produced catalysts, which revealed three unique peaks. The 530.3 eV signal was attributed to lattice oxygen species ( $O_L$ ), while the peak at 531.1 eV indicated the presence of  $O_V$ . The 532.2 eV peak was associated with OH species, specifically indicating the physical absorption of water on the surface ( $O_{OH}$ ) [199]. However, the  $O_L$  species in the NSZF-5 catalyst were difficult to identify. Table 4.2 summarizes the area ratios of  $O_V/(O_L+O_{OH})$ , which represent the concentration of  $O_V$  on the surface. The results showed a decreasing sequence: NSZF-15 (0.16) > NSZF-10 (0.11) > NSZF-5 (0.042). This suggests that the NSZF-15 catalyst produced more  $O_V$ .

| Catalysts | Ni 2p<br>$Ni^0/Ni$ | O 1s<br>$O_V/(O_L+O_W)$ | desorbed $CO_2$ amount<br>(mmol/g) |
|-----------|--------------------|-------------------------|------------------------------------|
| NSZF-3    | -                  | -                       | 0.063                              |
| NSZF-5    | 0.23               | 0.042                   | 0.083                              |
| NSZF-10   | 0.34               | 0.11                    | 0.081                              |
| NSZF-15   | 0.34               | 0.16                    | 0.122                              |
| NSZF-20   | -                  | -                       | 0.093                              |

Table 4.2: The surface compositions, and  $CO_2$  desorption amount of the fresh NSZF catalysts.

Moreover, the reducibility of the catalyst was investigated through  $H_2$ -TPR, and the results are presented in Figure 4.4 e. Typically, NiO is reduced to  $Ni^0$  in the presence of hydrogen. The decline in the peak observed at 300-450 °C indicates the existence of surface NiO particles exhibiting limited contact with the SZF. Conversely, the peak observed between 450-600 °C corresponds to NiO particles located within the pores, demonstrating significant interaction with the SZF [200]. Generally, the decline of some NiO species is intimately associated with the formation of peaks at different

temperatures. In the case of the NSZF catalysts, separate deconvoluted peaks were detected at various temperatures. The decrease of NiO species on the SZF surface is responsible for the peaks observed at temperatures lower than 400 °C. Conversely, the peaks detected approximately at 400 °C are related to the NiO reduction, which interacts with the SZF. Interestingly, the temperatures of the four reduction peaks were found to be greater at larger Ni contents in SZF. These observations originated in the high-temperature range. The NiO species interacting with the Si-O-Ni support is indicated by these peaks over a temperature of 500 °C, which are caused on by finely dispersed Ni particles inside the fibrous structure of SZF. Si-O-Ni formation may provide strong and persistent activity by preventing Ni sintering and catalyst deactivation during the DDRMRM. This is important because the MSI has a considerable impact on coke formation [201].

Furthermore, the DRM process depends significantly on the activation of CO<sub>2</sub> molecules. CO<sub>2</sub>-TPD is widely employed to evaluate the catalysts' ability to adsorb and dissociate CO<sub>2</sub> molecules, providing valuable information about their basic sites [200]. The strength of these basic sites can be studied by analyzing the CO<sub>2</sub> desorption peaks, as depicted in Figure 4.4 f. The NSZF catalysts showed distinct CO<sub>2</sub> desorption peaks, each of which represented a different kind of adsorption center. Below 200 °C, the OH species on the SZF surface gave rise to weak CO<sub>2</sub> adsorption sites. In the 200–350 °C range, Lewis acid-base site pairs gave rise to medium CO<sub>2</sub> adsorption centers. Low-coordination lattice oxygen (O<sup>2-</sup>) was found to be the source of strong adsorption centers over 350 °C. These catalysts revealed several types of basic sites such as weak, medium, or strong according on their strength. The formation of a

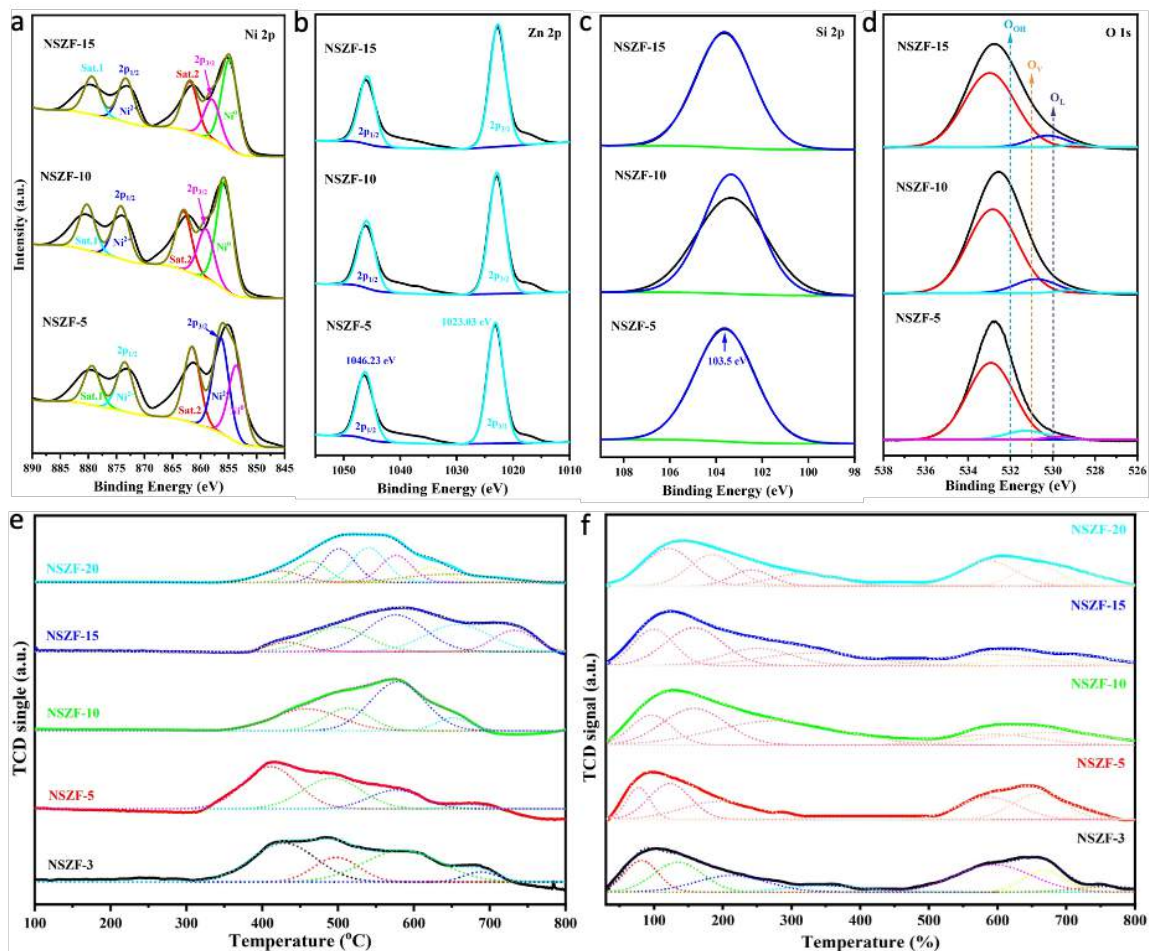


Figure 4.4: (a,b,c,d) XPS spectra of the fresh NSZF-5, NSZF-10, and NSZF-15 catalysts, (e) H<sub>2</sub>-TPR profiles, and (f) CO<sub>2</sub>-TPD profiles of the NSZF catalysts.

fibrous structure inside the catalysts aided the dispersion of Ni particles on the SZF surface, influencing both the strength and amount of CO<sub>2</sub> desorption, as well as the level of metallic loading. The quantity of CO<sub>2</sub> desorbed was computed and is detailed in Table 4.2. Significantly, the most medium-strength CO<sub>2</sub> adsorption sites (0.122 mmol/g) were found in NSZF-15 catalyst. This observation aligns with the earlier stated results, highlighting the exceptional performance of the NSZF-15 catalyst in the DRM process.

### 4.1.2 Catalytic performance

The catalysts were thoroughly tested to evaluate their performance, and the results are depicted in Figure 4.5. The conversions of  $\text{CO}_2$  and  $\text{CH}_4$ , as well as the  $\text{H}_2/\text{CO}$  ratio, increased significantly with temperature. This phenomenon is explained by the DRM process's endothermic nature. Overall, it was discovered that the conversion of  $\text{CO}_2$  and  $\text{CH}_4$  was quite similar. However, the conversion of  $\text{CO}_2$  was higher since the RWGS reaction was also taking place at low temperatures of DRM. Figure 4.5 a,b illustrate that the NSZF-10 catalyst, containing 10wt.% Ni, exhibited nearly the same  $\text{CH}_4$  conversion as the NSZF-15 catalyst, which had a higher Ni content, at 700 and 750 °C. Similarly, the  $\text{CO}_2$  conversion at these temperatures was also comparable between the catalysts. But out of all the catalysts examined, NSZF-10 and NSZF-20 both showed more  $\text{CO}_2$  conversion, particularly at temperatures lower than 800 °C. These findings suggest that the catalysts' surface was more active for the conversion of  $\text{CO}_2$  at these temperatures. Also, the TPR profiles revealed that a rise in the Ni amount led to a shift in the reduction peak towards higher temperatures. This shift was accompanied by higher peak intensities and a greater consumption of  $\text{H}_2$ . This indicates a stronger MSI for the NSZF-10 and NSZF-15 catalysts. On the other hand, the NSZF-3 and NSZF-5 catalysts exhibited the lowest reduction peak area and  $\text{H}_2$  consumption among all the catalysts. This can indicate that the silica shell of these catalysts was thicker, which made it harder for reactant molecules and  $\text{H}_2$  to reach the metal sites [201]. This investigation suggests that there exists an optimal Ni content for the SZF support. Additionally, at higher reaction temperatures, the  $\text{H}_2$  yield

surpasses the CO yield for all the catalysts, as presented in Figure 4.5 c. Moreover, Figure 4.5 d demonstrates that the NSZF-15 and NSZF-20 catalysts achieved higher conversion of CH<sub>4</sub> and H<sub>2</sub>/CO ratio among the catalysts. This occurrence can be attributed to the enhanced progression of the CH<sub>4</sub> decomposition (cracking) reaction on these catalysts, likely because of the larger size of the Ni nanoparticles [202]. Moreover, the H<sub>2</sub>/CO ratio was found to be less than unity at 700 °C, demonstrating the presence of the RWGS reaction [203]. However, at reaction temperatures exceeding 750 °C, the H<sub>2</sub>/CO ratio exceeded the unity. This indicated the occurrence of the CH<sub>4</sub> decomposition reaction on the catalyst, leading to an increase in H<sub>2</sub> yields.

In addition, the stability of the NSZF catalysts for DRM was tested at 750 °C for 40 h TOS, as illustrated in Figure 4.6. Notably, the catalytic performance of the NSZF-10 and NSZF-15 catalysts was exceptional, as indicated in Figure 4.6 a,b. These catalysts demonstrated stable CO<sub>2</sub> conversions of 60%, 74%, and 66%, respectively. Additionally, the NSZF-10 and NSZF-20 catalysts exhibited consistent CH<sub>4</sub> conversions of 82% and 87%, respectively (Figure 4.6 a). However, it should be noticed that the catalytic stability of the NSZF-3 catalyst declined after 35 h of TOS. This deterioration can be attributed to the limited active sites on the surface and increased Ni aggregation at the high operating temperature. Consequently, these factors led to coke deposition and catalyst deactivation [204]. Based on Figure 4.6 d, the trend of H<sub>2</sub> yield differed across different conversions. NSZF-15 catalyst showed the highest H<sub>2</sub> yield at 64%, while NSZF-3 catalyst exhibited the lowest yield. The RWGS reaction may be responsible for the decreased CO selectivity observed with the NSZF-3 catalyst. NSZF-5 and NSZF-20 catalysts demonstrated similar trends in H<sub>2</sub> and CO

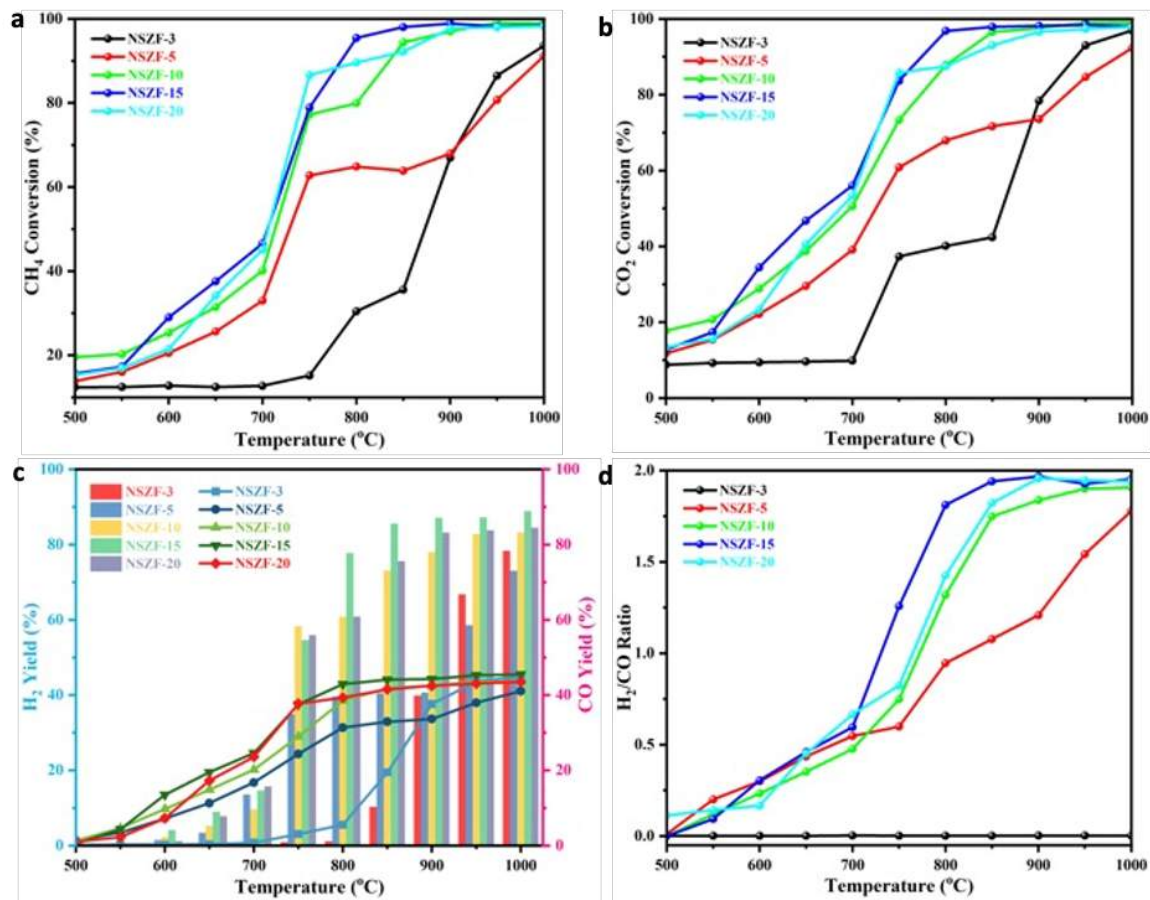


Figure 4.5: Catalytic activity of NSZF catalysts: (a) CH<sub>4</sub> conversion, (b) CO<sub>2</sub> conversion, (c) H<sub>2</sub> yield and CO yield, and (d) H<sub>2</sub>/CO ratio.

selectivity and yield, following the same pattern. Similarly, NSZF-10 and NSZF-15 catalysts also showed consistent trends and achieved the highest H<sub>2</sub> selectivity at 69%, resulting in an elevated H<sub>2</sub>/CO ratio as depicted in Figure 4.7 c. Furthermore, the H<sub>2</sub>/CO ratio for NSZF-3 catalyst was found to be less than unity, whereas the ratio for NSZF-5 and NSZF-20 catalysts remained close to unity during the initial 20 h of the reaction. The ratio ranged from 0.80 to 1.27, as shown in Figure 4.7. This range is suitable for the FTS, which involves synthesizing long-chain hydrocarbons. This difference may be attributed to the ability of NSZF-5 and NSZF-20 catalysts to disperse oxygen species on the surface [205]. During the catalytic evaluation, it was predictable that simultaneous secondary reactions would occur. The H<sub>2</sub>/CO ratio revealed that the increase in the syngas ratio during the reaction was driven by two concurrent reactions. Firstly, methane decomposition resulted in the cracking of CH<sub>4</sub> to produce 2H<sub>2</sub>. Secondly, CO disproportionation occurred, where CO reacted to produce CO<sub>2</sub> and carbon. In addition to affecting the syngas ratio, these secondary reactions also generated carbonaceous species that had a negative impact on the catalytic activity. Furthermore, the presence of these carbonaceous species was found to be detrimental to the overall performance of the catalysts. However, in the first hours of the reaction, NSZF-3, NSZF-5, and NSZF-20 exhibited a syngas ratio lower than unity. This was caused by the RWGS reaction, which led to a decrease in the syngas ratio. As time progressed, the syngas ratio showed growth and approached unity, indicating favorable thermodynamics [206]. NSZF-10 exhibited excellent activity, which can be attributed to the abundance of active sites provided by the mesoporous and microporous structure of the fibrous temple support. The characterization results provided insights

into the catalyst's structure, revealing a uniformly dispersed and thinner crystallite of NiO throughout the SZF material. This structural feature likely contributed to the enhanced catalytic performance of NSZF-10. On the other hand, NSZF-15 exhibited a high conversion of CH<sub>4</sub> and CO<sub>2</sub> initially. However, the conversion of CO<sub>2</sub> started to decline after the first few hours of the reaction due to CO disproportionation. In FESEM and TEM analysis, NSZF-15 showed more accumulation of Ni onto the SZF. The accumulation of NiO within the SZF resulted in increasing engagement of NiO, thereby enhancing the environmental basicity of the catalysts [207]. Overall, the different catalysts exhibited varying behavior, with NSZF-10 showing preferable activity, NSZF-15 demonstrating high conversion initially but declining CO<sub>2</sub> conversion, and NSZF-3, NSZF-5, and NSZF-20 exhibiting a lower syngas ratio initially due to the RWGS reaction. The unique properties and characteristics of each catalyst played a significant role in their performance and stability.

### 4.1.3 Spent catalysts characterization

TEM, Raman, TGA, and XRD were performed to study the coke deposition after the reaction, as carbonaceous species formation is unavoidable during DRM [208]. Figure 4.8 illustrates the presence of circular-shaped dark spots on the SZF structure, representing the distribution of Ni particles, while also displaying visible depositions of amorphous carbon, whiskers, and CNTs in the spent catalysts [209]. As observed in Figure 4.8(b-3), the graphitic whiskers and CNTs showed crystal structures with lattice fringes. Interestingly, no morphological changes were observed in the catalysts after 40 h of DRM for NSZF-3, NSZF-10, and NSZF-15, indicating the preserved fibrosity

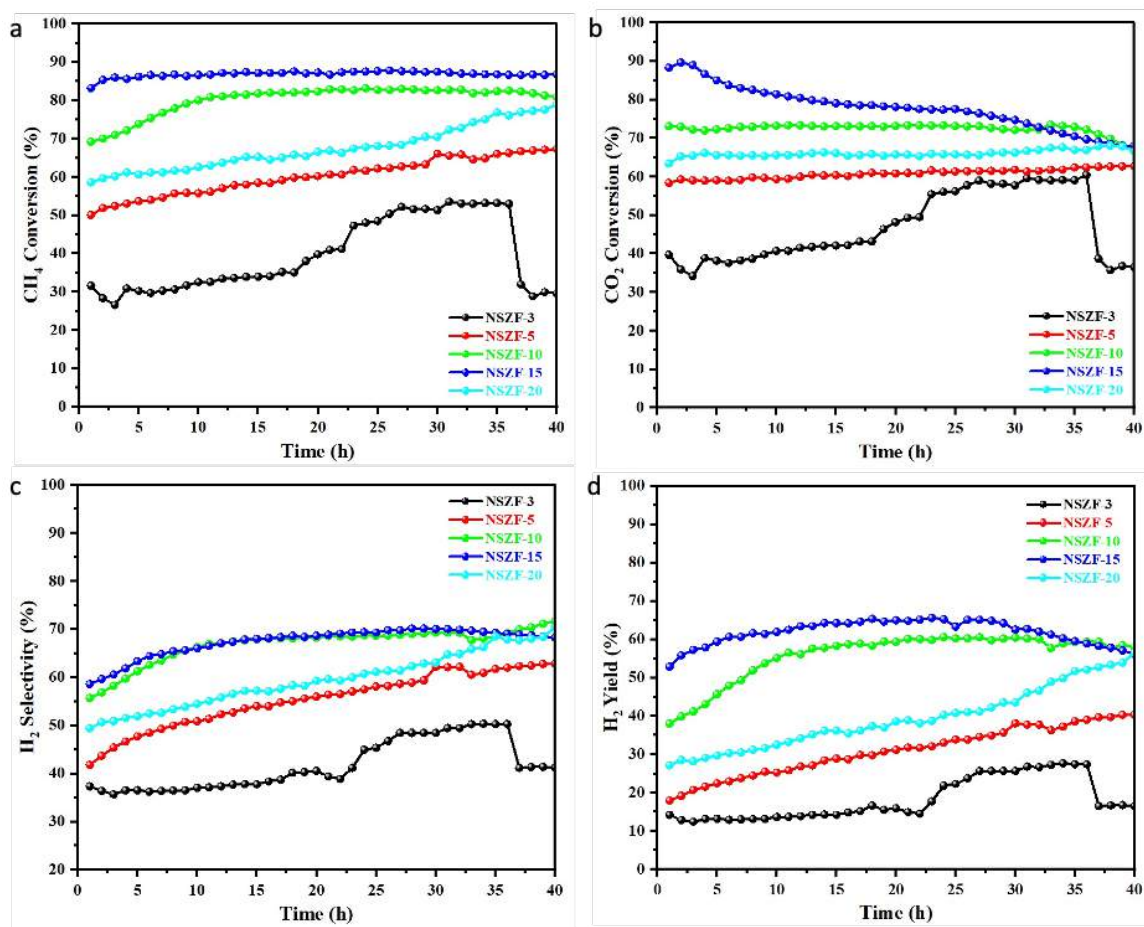


Figure 4.6: Catalytic stability of NSZF catalysts: (a) CH<sub>4</sub> conversion, (b) CO<sub>2</sub> conversion, (c) H<sub>2</sub> selectivity, and (d) H<sub>2</sub> yield (conditions: P=1 atm, T=750 °C, GHSV=12000 mLg<sup>-1</sup><sub>cat</sub>.h<sup>-1</sup>, t=40 h).

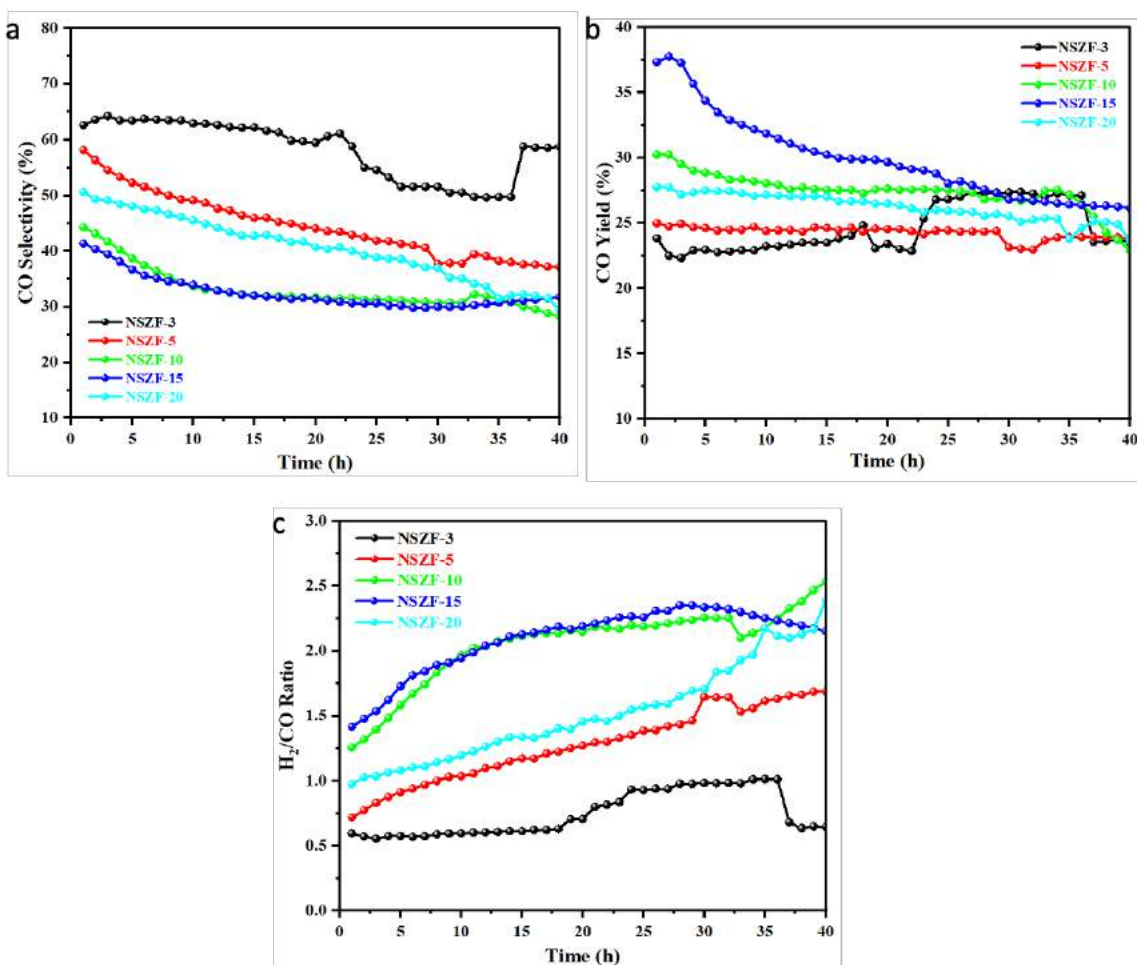


Figure 4.7: Catalytic stability of NSLF catalysts: (a) CO selectivity, (b) CO yield, (c) H<sub>2</sub>/CO ratio (conditions: P=1 atm, T=750 °C, GHSV=12000 mLg<sup>-1</sup><sub>cat</sub>.h<sup>-1</sup>, t=40 h).

of SZF. The distribution of Ni particles in NSZF-10 was centered near the SZF core, as shown in Figure 4.8c. Most of the Ni particles in NSZF-15 were found on the SZF surface, as shown in Figure 4.8e. The Ni lattice fringes with a 0.204 nm lattice spacing, corresponding to Ni (111), were observed in both samples within the considered area [210]. Additionally, NSZF-10 and NSZF-15 displayed two different lattice fringes, indicating the presence of whiskers and CNTs with varying degrees of graphitization. Notably, the impregnated sample exhibited significant agglomeration of Ni particles, resulting in larger particle sizes due to sintering caused by migration of Ni atomic or crystallite, as also observed in the NSZF-3 and NSZF-15 catalysts. This observation was additionally supported by the XRD of the spent catalysts (Figure 4.9c). Figure 4.8c (NSZF-10) illustrates the presence of disordered amorphous carbon surrounding the Ni NPs. This carbon type is known for its minimal catalytic deactivation and easy gasification in the air, resulting in the production of additional CO. This means that long-term DRM has a low probability of carbon accumulation, which is responsible for the small amount of carbon deposition that appears after 40 h of reaction. The Raman spectra (Figure 4.9a) confirm that the carbon production was more significant in the catalysts, with crystalline carbon deposits appearing in fewer regions of the Ni-loaded catalyst. As demonstrated by Figure 4.6(a,b), the noticeable deactivation of NSZF-3 after 37 h was caused by the development of stable and ordered carbon deposits and decreased sintering resistance. The catalyst is more prone to deactivation because of the increased production of graphitic carbon [211]. The increased activity of the NSZF-10 catalyst with no morphological changes can be explained by the differences in sintering resistance between the catalysts, shown by TEM images.

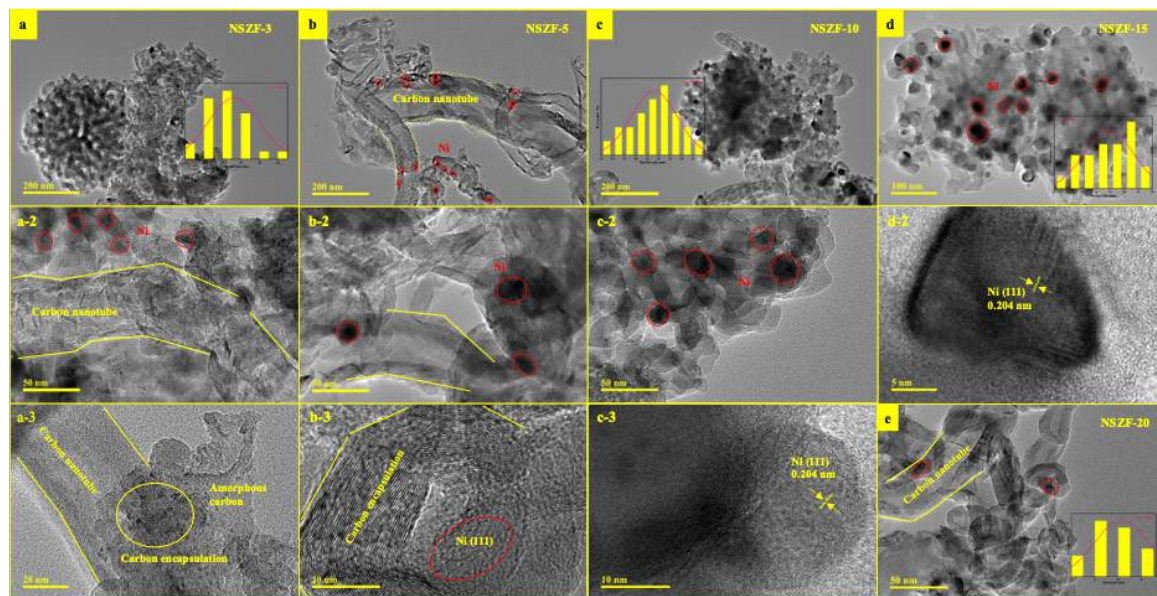


Figure 4.8: TEM images of the spent catalysts after 40 h reaction time.

Figure 4.9a shows the Raman spectra of the spent catalysts, which investigate carbon deposition on the NSZF catalysts. There are two different bands present: the disorder-induced band (D-band) at  $1342\text{ cm}^{-1}$ , which is produced by amorphous carbon, and the C-C stretching in the graphite carbon band (G-band) at  $1591\text{ cm}^{-1}$  [212]. The degree of defects in the graphite carbon has been demonstrated by the ratio ( $I_G/I_D$ ) of the G-band to the D-band. A higher degree of graphitic carbon formation is indicated by an  $I_G/I_D$  ratio greater than unity, whereas a smaller ratio indicates a smaller amount of graphitic carbon production. Significantly, the NSZF-10 and NSZF-15 catalysts displayed the least graphitic carbon deposition, as evidenced by the  $I_G/I_D$  values illustrated in Figure 4.9a [195]. This indicates that NSZF-10 and NSZF-15 can effectively reduce carbon accumulation, highlighting their resistance to graphitic carbon compared to the other catalysts. To further investigate coke deposition on the spent catalysts, TGA analysis was carried out, as depicted in Figure

4.9b. NSZF-3, NSZF-5, and NSZF-10 showed a weight decrease starting at 100 °C, indicating the presence of physisorbed molecules. This weight loss could be associated with the release of entrapped water within the catalyst’s framework or the loss of physisorbed water produced during the DRM and RWGS reaction [213]. The weight of the spent catalysts initially increased until reaching 500 °C because of Ni partial oxidation. The catalysts then lost weight between 390-700 °C, indicating the removal of graphitic and amorphous carbon produced during the reaction. Notably, NSZF-15 exhibited the least weight loss at higher temperatures, suggesting lower graphitic carbon deposition. This observation aligns with the Raman analysis and can be primarily attributed to the abundance of  $O_V$  and medium strength  $CO_2$  adsorption centers present in NSZF-15. These findings strongly indicate minimal carbon deposition and stability against carbon accumulation in NSZF-15. Figure 4.9c displays the XRD results of the spent catalysts. In all cases, characteristic peaks corresponding to ZnO and metallic Ni were observed, indicating the presence of these components in the spent catalysts. However, the metallic Ni peaks in the NSZF-15 and NSZF-20 catalysts appeared slightly sharper, suggesting partial migration and aggregation of metallic Ni during the DRM process. Additionally, new peaks attributed to graphitized carbon were observed, with the weakest intensities in NSZF-15 because of the limited quantity of carbon on the catalytic surface. NSZF-20 exhibited the strongest intensities, indicating higher crystallinity compared to its fresh state and implying visible metal sintering through XRD analysis [214]. The presence of small  $Ni^0$  particles in NSZF-10 indicates less pronounced Ni sintering, resulting in improved catalytic stability in the DRM process.

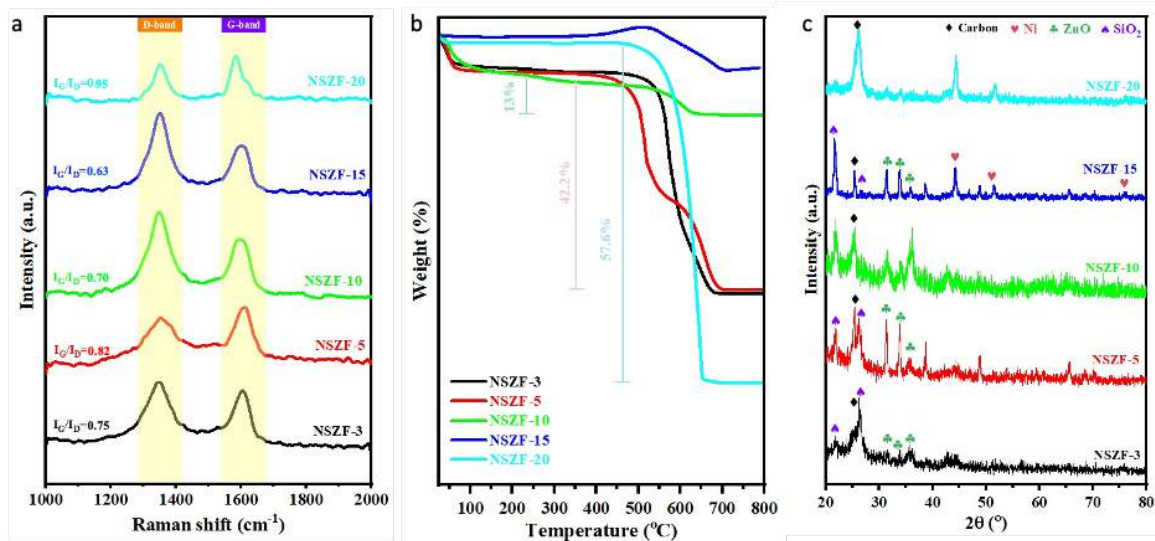


Figure 4.9: (a) Raman spectra, (b) TGA profiles, and (c) XRD patterns of all the spent NSZF-x catalysts.

## 4.2 Ni-based Silica Lanthanum-Oxide Catalysts

Herein, we fabricated silica lanthanum oxide supported nickel (NSLF-10) with a core-fibrous shell framework and silica lanthanum oxide supported nickel composite (NSL-C), based on the use of commercial lanthanum oxide and silica with 10 wt.% Ni over the both supports. The role of the interplaying morphology was investigated to enhance textural properties and surface area, thereby improving the performance of the DRM reaction. These physicochemical properties of the developed catalysts were investigated using different characterization techniques including N<sub>2</sub> adsorption-desorption and TEM and others. The NSLF-10 exhibited outstanding CO<sub>2</sub> and CH<sub>4</sub> conversions in the DRM reaction and the stability up to 22 h. The spent catalysts were studied by TEM, TGA, and Raman spectroscopy to analyze the shapes, types, and quantities of carbon deposits.

### 4.2.1 Fresh catalysts characterization

Figure 4.10 displays the TEM micrograph along with the corresponding NiO particle sizes of NSLF-10 and NSL-C. In Figure 4.10b, it is observed that the Ni deposition on SLF (Figure 4.10a) preserved the initial round structure of SLF, with fibers loaded and progressively increasing radially outward. However, distinct distributions and sizes of NiO NPs at the silica fiber structure, shown by the darkish and contrasting spots, were found for NiO loading on SLF. The average particle length of NiO is about 14 nm. These NiO NPs exhibited high dispersion over SLF, predicted to enhance catalytic performance throughout the reaction. Conversely, a rise in the average size of NiO NPs was observed on  $\text{SiO}_2\text{-La}_2\text{O}_3$ , 25 nm, as depicted in Figure 4.10e. This may be attributed to the agglomeration of NiO on the  $\text{SiO}_2\text{-La}_2\text{O}_3$  composite. Importantly, NSLF-10 exhibited even more remarkable NiO distributions, consistent with the findings by the  $\text{H}_2$ -TPR outcomes that the SMSI exhibited by NSLF-10 and the existence of the fibers amorphous  $\text{SiO}_2$  structure in the shell of SLF as illustrated by SAED pattern of NSLF-10 (Figure 4.10c). Moreover, the unique hierarchical pore structure of the SLF provided more intracapsular porosity for optimal NiO distribution. This uniform dispersion of NiO particles proves beneficial in reducing coke formation, as it encourages the transfer of CNTs to the catalyst interface, facilitating their interaction with the surface oxygen network. Furthermore, the particle size, NiO distribution, and composition of NSLF-10 and NSL-C were confirmed and demonstrated more using SEM-EDX, respectively as in Figure 4.11. The SLF exhibited a thick surface with prominent lumps, as shown in Figure 4.11(a,b). The surface roughness can be at-

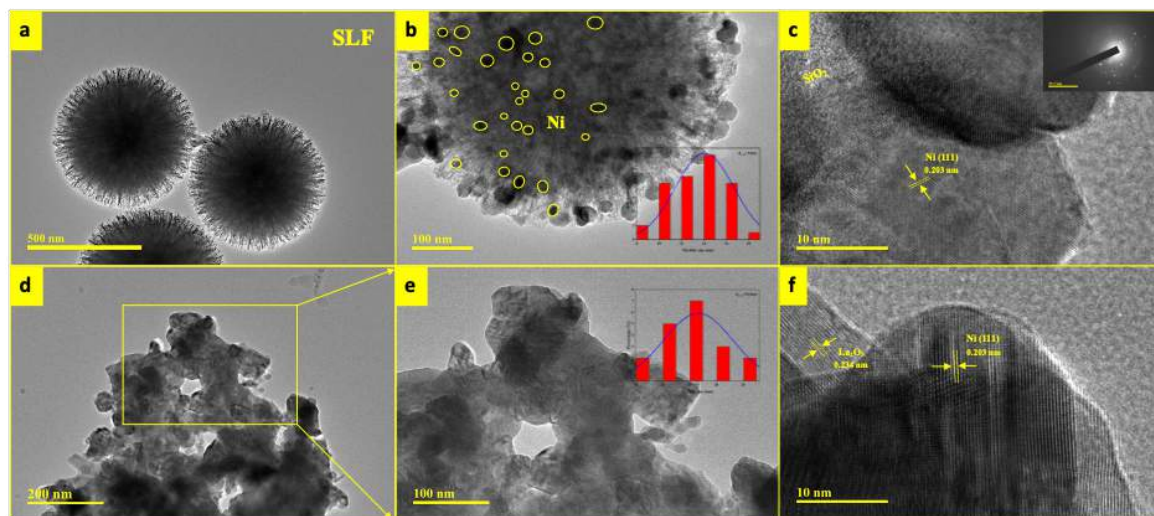


Figure 4.10: TEM images of the prepared NSLF-10 (a,b,c) and NSL-C (d,e,f).

tributed to the interparticle pores and fibrous morphology of the pristine SLF, where lumps observed indicate the NiO NPs dispersion. Moreover, EDS mapping (Figure 4.11c) showed a uniform distribution of high-intensity NiO elements on the SLF catalyst surface. This well-dispersed NiO indicates multiple accessible active sites on the catalysts. However, SEM-EDX images of the NSL-C catalyst are presented in Figure 4.11(d,e). The laminar structure resulting from the combination of commercial  $\text{SiO}_2$  and  $\text{La}_2\text{O}_3$  was observed. The morphological integrity of SLF remained intact after the addition of NiO NPs, as shown by the TEM image of the NSLF-10 catalyst. This structure closely resembled SLF without significant differences, as observed in previous studies. Therefore, this unique structure is believed to significantly enhance the hetero-catalytic efficiency. This improvement is due to the unique access of  $\text{CO}_2$  to the minimal dispersion constraint and few active sites, allowing a maximum rate of reaction [215].

Figure 4.12a displays the XRD diffractograms of NSL-C and NSLF-10, which have

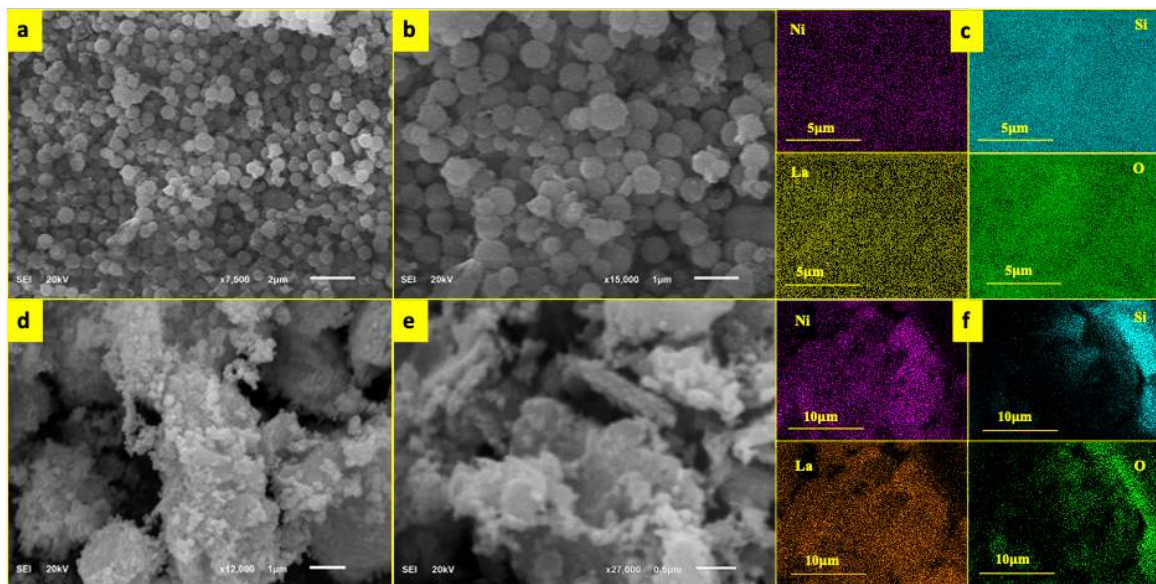


Figure 4.11: SEM micrographs and corresponding elemental mapping of NSLF-10 and NSL-C catalysts.

been used to investigate the phases and crystal structures of the catalysts. Both catalysts showed a broad and extreme band at  $2\theta$  in the range of  $20\text{--}30^\circ$ , generally indicative of the amorphous  $\text{SiO}_2$  [216]. The broad peak at  $22.4^\circ$  signifies the amorphous nature of the  $\text{SiO}_2$  [217]. Additionally, the  $\text{La}_2\text{O}_3$  peaks were observed and matched with COD card no. 00-153-1467. Nevertheless, the peaks associated with the phases of  $\text{La}_2\text{O}_3$  between  $60^\circ$  and  $70^\circ$  in NSLF-1 had not been observed, because of the formation of  $\text{SiO}_2$  shells [218]. Small shifts and reductions in the intensities of the diffraction peaks may be ascribed to the impact of  $\text{SiO}_2$  encapsulating  $\text{La}_2\text{O}_3$ . This means that the introduction of  $\text{SiO}_2$  has a minimum effect on the lattice shape of  $\text{La}_2\text{O}_3$ . Notably, the peak was detected at  $2\theta = 20.89^\circ$  (100) and  $26.72^\circ$  (011) in NSL-C, corresponding to the cristobalite low-kind  $\text{SiO}_2$  (COD card no. 00-153-2512) [218]. This arises from the use of different precursors in the synthesis of SLF and  $\text{SiO}_2\text{-La}_2\text{O}_3$ , in which TEOS serves as the silica source for SLF, and pure  $\text{SiO}_2$  is

the source of silica in the  $\text{SiO}_2\text{-La}_2\text{O}_3$  support. Furthermore, we used  $\text{N}_2$  sorption technique to analyze the pore size, surface area, and pore volume, and correlate the textural properties of the catalysts with the catalytic DRM performance.

Figure 4.12b presents the FTIR patterns of the synthesized catalysts in a range of wavenumbers from 400 to  $4000\text{ cm}^{-1}$ . In the range of  $400\text{--}1400\text{ cm}^{-1}$ , significant peaks were analyzed, representing the presence of a siliceous framework where silicon reacts with other atoms (e.g.,  $\text{Si-OH}$ ,  $\text{Si-O}$ ,  $\text{Si-O-La}$ ,  $\text{Si-O-Si}$ , and  $\text{La-O}$ ). The NSLF-10 catalysts exhibited prominent bands at  $1090.5$ ,  $970$ ,  $807.9$ , and  $470.2\text{ cm}^{-1}$ , that can be attributed to the bending vibrations of the asymmetric  $\text{Si-O-Si}$  network, symmetric  $\text{Si-O-Si}$ ,  $\text{Si-O-Si}$  bending, and  $\text{La-O}$  stretching, respectively [219]. A distinct and extended peak at  $1090.5$  and  $470.2\text{ cm}^{-1}$  was analyzed in the FTIR spectrum of NSLF-10, indicating the formation of a well-developed mesoporous network. This observation aligns with the SEM results depicted in Figure 4.11. The peak wavelengths observed in SLF were greater than those observed in NSL-C. This finding suggests that SLF has stronger bonds between silicon and oxygen atoms, as well as  $\text{-OH}$  molecules. The presence of the siliceous fibrous component surrounding SLF enhances the production of terminal silanol groups to a greater extent than the contribution of the siliceous body in NSL-C.

The  $\text{N}_2$  adsorption-desorption isotherms and pore distributions of NSLF-10 and NSL-C catalysts are illustrated in Figure 4.12 (c,d). The sorption isotherm of NSLF-10 showed a type IV isotherm, indicating mesoporosity of the structure [220]. The SLF support and NSLF-10 catalyst displayed capillary condensation, showing the presence of interparticle and intraparticle voids. The formation of sizable pore volumes within

the catalysts becomes evident from the advent of a type H<sub>3</sub> hysteresis loop at high pressures. The formation of mesopores became verified by the hysteresis loops found in the SLF. Meanwhile, the reduction in the amount of adsorbed N<sub>2</sub> inside the presence of NSLF-10 and NSL-C indicated the embedding of NiO onto the supports. Table 4.3 presents a comprehensive overview of the textural properties of the catalytic materials. The synthesized fibrous structure used in this study exhibited a surface area of 362 m<sup>2</sup>g<sup>-1</sup>, due to the presence of interparticle and intraparticle voids. This increased surface area allows for higher dispersion of the active metal. Upon loading with Ni, the surface area of NSLF-10 becomes 192 m<sup>2</sup>g<sup>-1</sup>, considerably greater than the NSL-C. Moreover, the increased Ni coverage on SLF indicates an optimized distribution, and the effectiveness of the fibrous catalyst in improving the surface area. Nevertheless, the decrease observed in the surface area of NSLF-10 in comparison to SLF may be attributed to the partial pores' blockage due to the Ni loading. However, it is important to highlight that this blockage did not affect the existing pore structure, as the pore size remained consistent for both catalysts [221].

| Catalysts | Surface area<br>(m <sup>2</sup> /g) | Total pore volume<br>(cm <sup>3</sup> /g) | Pore size<br>(nm) |
|-----------|-------------------------------------|-------------------------------------------|-------------------|
| NSLF-3    | 192                                 | 0.241                                     | 7.46              |
| NSL-C     | 122                                 | 0.799                                     | 26.05             |

Table 4.3: Textural properties of the prepared catalysts.

The reducibility and MSI of the produced Ni-based catalysts were examined through H<sub>2</sub>-TPR analysis, as illustrated in Figure 4.13. The reduction profiles of NSL-C also displayed a wide peak in the range of 400-600°C, indicating the NiO reduction and highlighting the distinct MSI [222]. Furthermore, it is evident that the

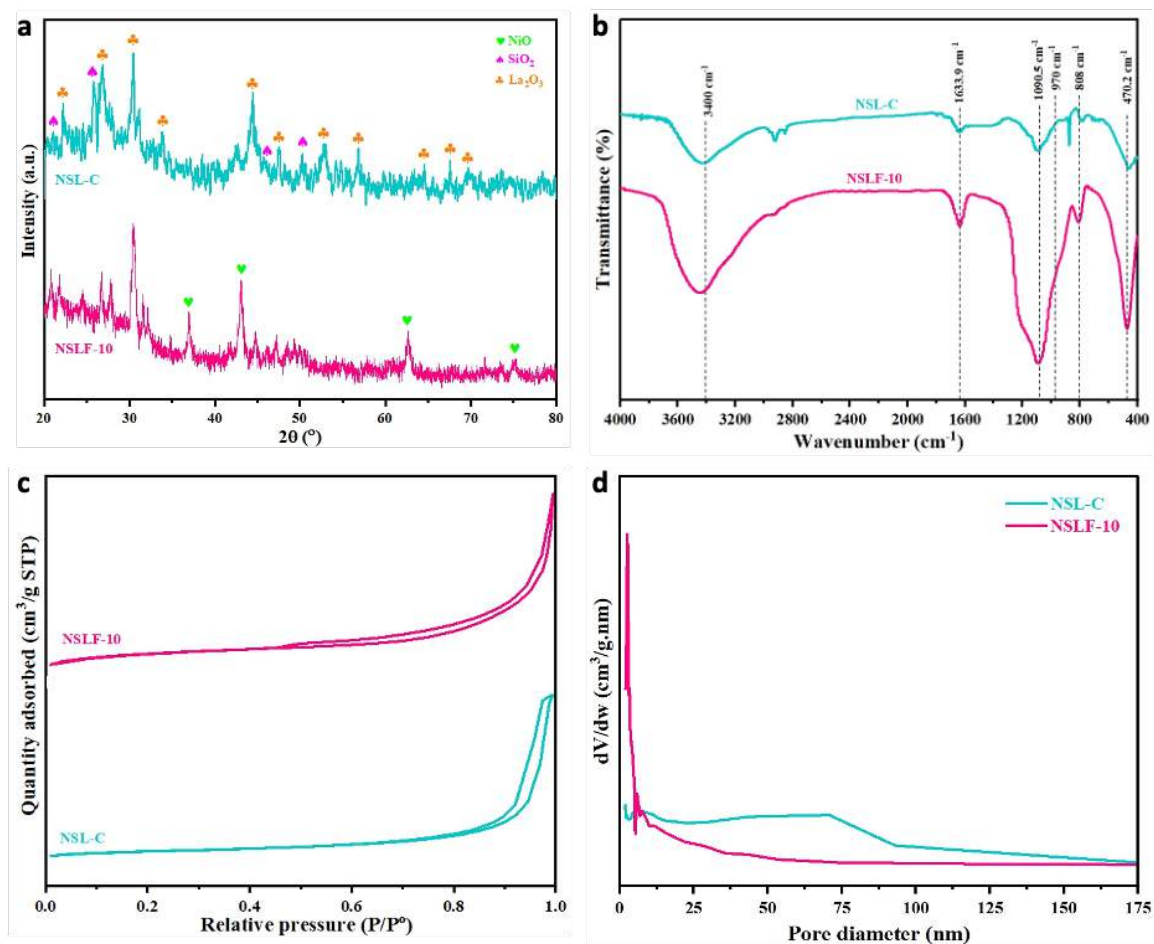


Figure 4.12: (a) XRD diffractogram, (b) FTIR patterns, (c)  $\text{N}_2$  adsorption-desorption isotherms, (d) pore size distributions of the prepared catalysts.

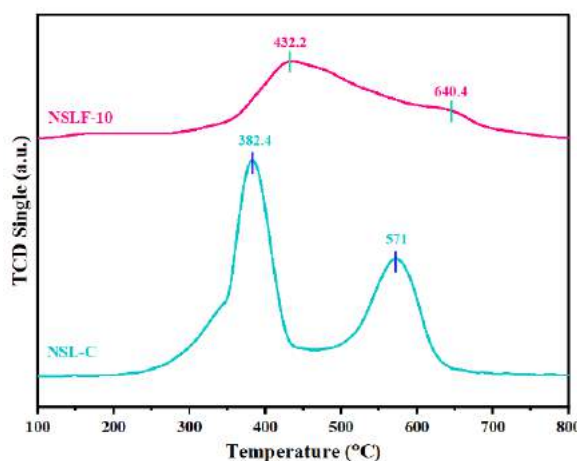


Figure 4.13: H<sub>2</sub>-TPR profile of the prepared catalysts.

NSL-C second reduction peak is significantly lower, indicating that the incorporation of SiO<sub>2</sub> has resulted in strong interaction with La<sub>2</sub>O<sub>3</sub>, resulting in the production of a complex oxide. This interaction weakens the NiO and La<sub>2</sub>O<sub>3</sub> strong interaction. Also, the TPR profile of NSLF-10 similarly shows two-phase NiO reduction peaks. Notably, the significant intensity of the reduction peak at 432°C is due to the reduction of bulk NiO into active Ni<sup>0</sup> species, that are firmly connected with the exterior SLF fibers. This indicates that NSLF-10 possesses superior reducibility compared to NSL-C. This characteristic provides a higher number of active Ni sites for the reaction, thereby increasing the catalytic activity. In addition, the second reduction peak of NSLF-10 shows a slight shift to a greater temperature (above 600°C). It suggests that several NiO particles are distributed inside the interior dendrimer fibers of SLF, exhibiting a SMSI and strong bonding [223].

### 4.2.2 Catalytic performance

Figure 4.14 reveals that the NSLF-10 catalysts exhibited higher catalytic efficiency for DRM than the NSL-C, which can be attributed to their enhanced textural properties, uniform Ni distribution, and morphological structure. This improvement is evident from the SEM image, which demonstrates an expanded distribution of Ni. The increased porosity and surface area facilitate the presence of active reaction sites and enhance the reactants' mass transfer. The textural properties, involving pore volume, pore size, and surface area, are crucial factors influencing catalyst activity. In this context, the properties of SLF, such as its pore volume, pore size, and surface area, contribute to the presence of active species that enable the resistance to catalyst deactivation [224]. Therefore, the large surface area of SLF allows increased oxygen storage on the catalyst, enabling the carbon oxidation to CO while forming intermediate carbonate species on reducible basic supports. This process effectively prevents the formation of coke, which is a negative consequence of this catalytic process. Figure 4.14a demonstrates the remarkable catalytic stability of both NSLF-10 and NSL-C catalysts, with no signs of deactivation observed within a 22-h TOS under reaction conditions. However, the NSL-C catalyst exhibited an increasing yield of  $H_2$  and  $H_2/CO$  ratio over time, eventually reaching 47% and high  $H_2/CO$  ratio, respectively. In contrast, the NSLF-10 catalyst showed superior catalytic effectiveness, consistently maintaining high conversion for  $CO_2$  and  $CH_4$ . Specifically, the NSLF-10 catalyst achieved remarkable conversions of 83% for  $CO_2$  and 85% for  $CH_4$ , surpassing the performance of the NSL-C catalyst, which achieved conversions of 64% for  $CO_2$

and 72% for  $\text{CH}_4$ . The higher performance of NSLF-10 over NSL-C is because of the existence of additional active sites given by the support's mesoporous and microporous fibrous. In contrast, the comparatively lower catalytic efficiency observed with NSL-C can be attributed to the formation of carbonaceous species and the potential sintering of the metal particles during the reaction. In Figure 4.14b, the CO yield follows a similar trend to the conversions, with NSL-C showing the lowest CO and highest  $\text{H}_2$  yields. However, there is an exception with the  $\text{H}_2$  yield analyzed for both NSLF-10 and NSL-C catalysts, which can be attributed to concurrent secondary reactions taking place. Generally, the  $\text{H}_2$  and CO yields for NSLF-10 is 65% to 37%, respectively, indicating stable performance throughout the reaction period. This is due to the excellent access of reactants on the NSLF-10 catalyst, which possesses good structural stability and an abundance of meso- and micro-pores. The inferior performance of NSL-C is due to the larger size of Ni particles and the accumulation of Ni on the  $\text{SiO}_2\text{-La}_2\text{O}_3$  support. In contrast, the superior performance of NSLF-10 can be explained by the improved MSI resulting from the Ni crystallites' confinement effect inside the support framework. However, the rise in the syngas ratio is primarily attributed to the simultaneous occurrence of CO disproportionation,  $\text{CH}_4$  cracking, and WGS reaction. the occurrence of  $\text{CH}_4$  cracking can lead to higher  $\text{H}_2$  production during the reaction, as observed in both catalysts with a molar ratio of  $\text{H}_2/\text{CO} > 1$ , as shown in Figure 4.14c. This higher amount of  $\text{H}_2$  can result in increased carbon deposition, especially after extended TOS. The incorporation of  $\text{La}_2\text{O}_3$  as a co-support with  $\text{SiO}_2$  helps impede the growth of RWGS reaction and enhances the selectivity of  $\text{H}_2$ . The improved  $\text{CH}_4$  conversion can be attributed to the effective production

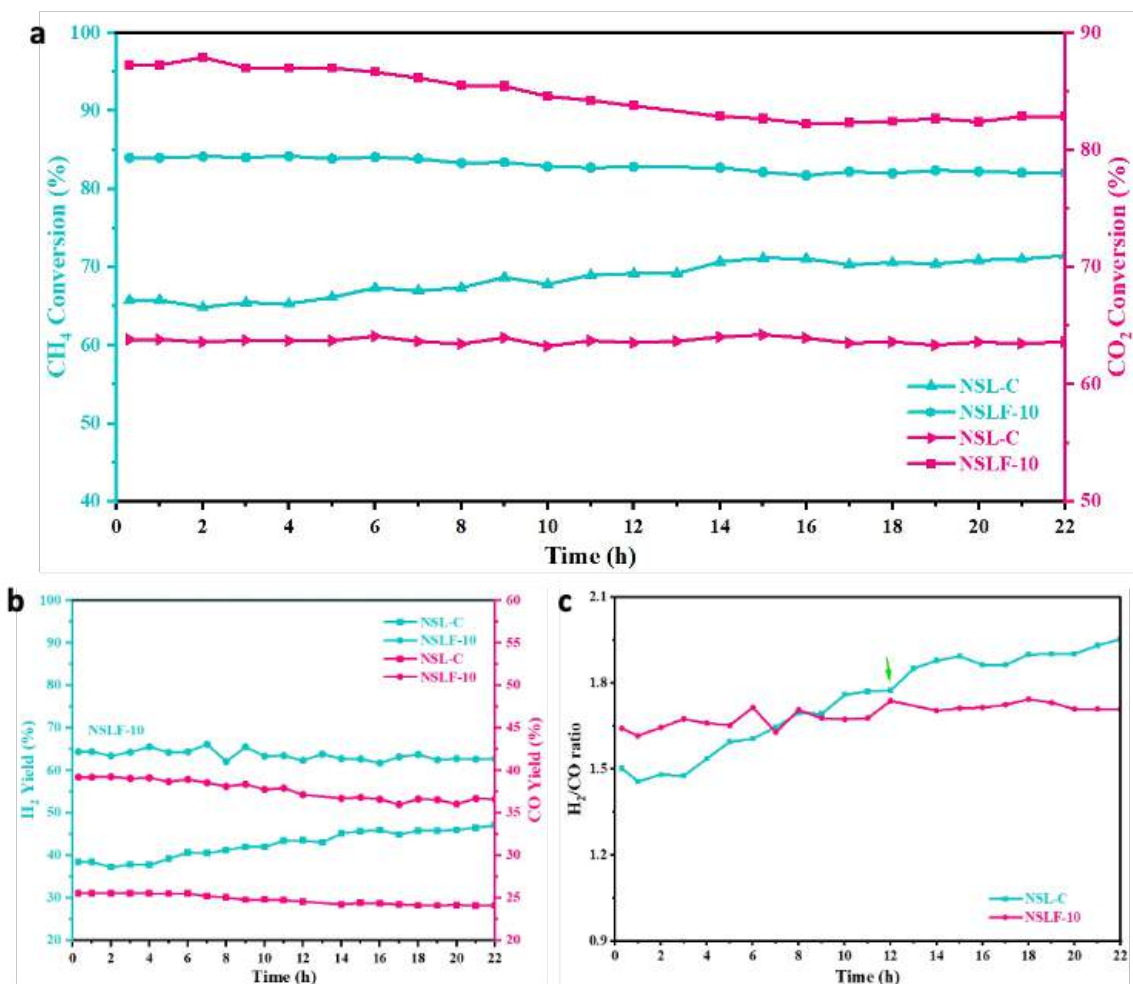


Figure 4.14: Catalytic performance over the catalysts (conditions:  $\text{CO}_2/\text{CH}_4=50/50$ ,  $\text{GHSV}=12000 \text{ mL.g}_{\text{cat}}^{-1}\text{h}^{-1}$ ,  $P=1 \text{ atm}$ ,  $T=750^\circ\text{C}$ ,  $t=22 \text{ h}$ ): (a)  $\text{CO}_2$  and  $\text{CH}_4$  conversion, (b)  $\text{H}_2$  and  $\text{CO}$  yield, and (c)  $\text{H}_2/\text{CO}$  ratio.

of active sites, as demonstrated in the  $\text{H}_2$ -TPR profile. The bulk formation of these active sites triggers  $\text{CH}_4$  and prevents recombination of  $\text{C}_x\text{H}_x$  through further dissection. The higher  $\text{H}_2/\text{CO}$  ratio indicates the presence of  $\text{CH}_4$  cracking, the Boudouard reaction, or the WGS reaction. These reactions typically take place on Ni active sites and can lead to their blockage.

### 4.2.3 Spent catalysts characterization

Figure 4.15a displays the Raman spectra of the NSLF-10 and NSL-C catalysts after undergoing the DRM process. These spectra provide valuable information regarding the presence of various carbon species. The signal at  $1341\text{ cm}^{-1}$  (D-band) is linked to induced-disordered Raman scattering caused by  $\text{sp}^3$  carbon atoms positioned at the disordered and defected sites. The peak at around  $1597\text{ cm}^{-1}$  (G-band) on the other hand, was linked with the pairs of  $\text{sp}^2$  carbon atoms having in-plane bond-stretching motion forming graphitic rings [225]. The  $I_D/I_G$  ratio is commonly utilized to represent the graphitization degree of carbon species, with a lower ratio indicating a larger degree of order in the carbon structure. In the spent catalysts, the  $I_D/I_G$  ratio of NSL-C after 22 h was 1.06, representing a greater graphitization degree than NSLF-10, which had an  $I_D/I_G$  ratio of 1.31. However, it can be analyzed that the catalyst' graphitization degree did not improve much during the period of the reaction. The findings of this study reveal that the catalyst has successfully established a dynamic equilibrium between the disordered graphitic and amorphous carbon forms. This equilibrium effectively prevents added carbon aggregation and transformation into more stable carbon deposits [226]. TGA was conducted in air to evaluate the amount of carbon deposit on the catalytic surface during the reaction, as shown in Figure 4.15b. TGA curves show two regions;  $250^\circ\text{C}$  -  $550^\circ\text{C}$ , in which the spent NSL-C gained weight due to Ni oxidation. In the range of  $550^\circ\text{C}$  -  $800^\circ\text{C}$ , the spent catalysts show weight loss due to the removal of deposited carbon facilitated by oxygen. The weight loss observed over the NSL-C catalyst exceeded that of the NSLF-10 catalyst.

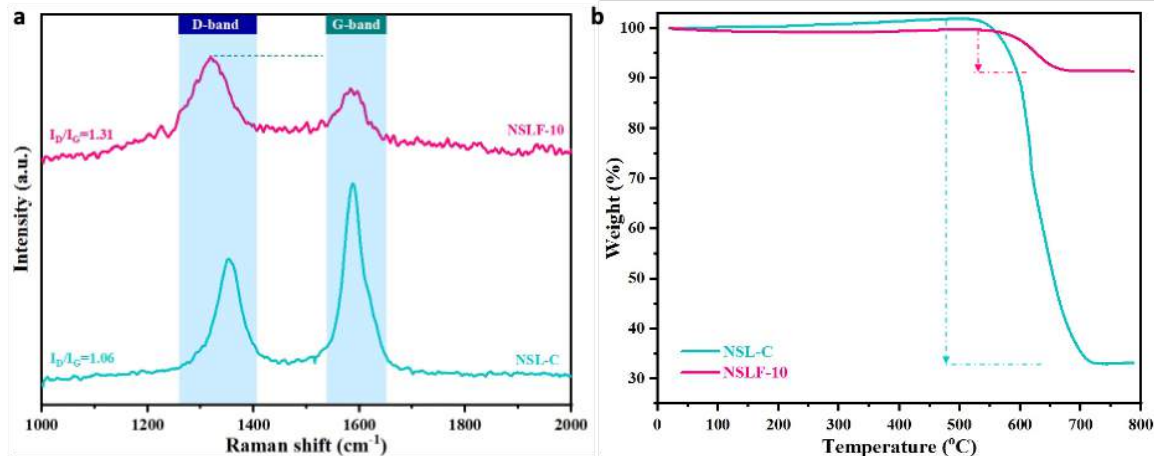


Figure 4.15: (a) Raman spectroscopy, and (b) TGA curves of the spent catalysts.

Furthermore, the elimination of deposited carbon from NSL-C necessitated higher temperatures. This observation suggests the formation of inert deposited carbon over NSL-C, rendering it more challenging to remove. Consequently, the NSLF-10 catalyst demonstrates high thermal stability and carbon formation resistance compared to NSL-C.

Figure 4.16 (a,b) presents the TEM micrographs, indicating the presence of amorphous carbon and CNTs in both NSLF-10 and NSL-C catalysts after 22 h of reaction. The observed CNTs exhibited closed and open ends, having Ni particles located at the tip. This type of carbon presented minimum or no deactivation and can be rapidly gasified in the occurrence of oxygen, producing extra CO. As a result, the probability of aggregation was confined in the prolonged DRM process. However, the TEM results indicated the occurrence of amorphous carbon, CNTs, and whiskers within the spent NSL-C catalyst. Significantly, an increased formation of graphitic carbon corresponded to an expanded susceptibility of the catalyst to deactivation [227]. As noted in the case of NSL-C catalyst, during the reaction period the H<sub>2</sub> yield increased this

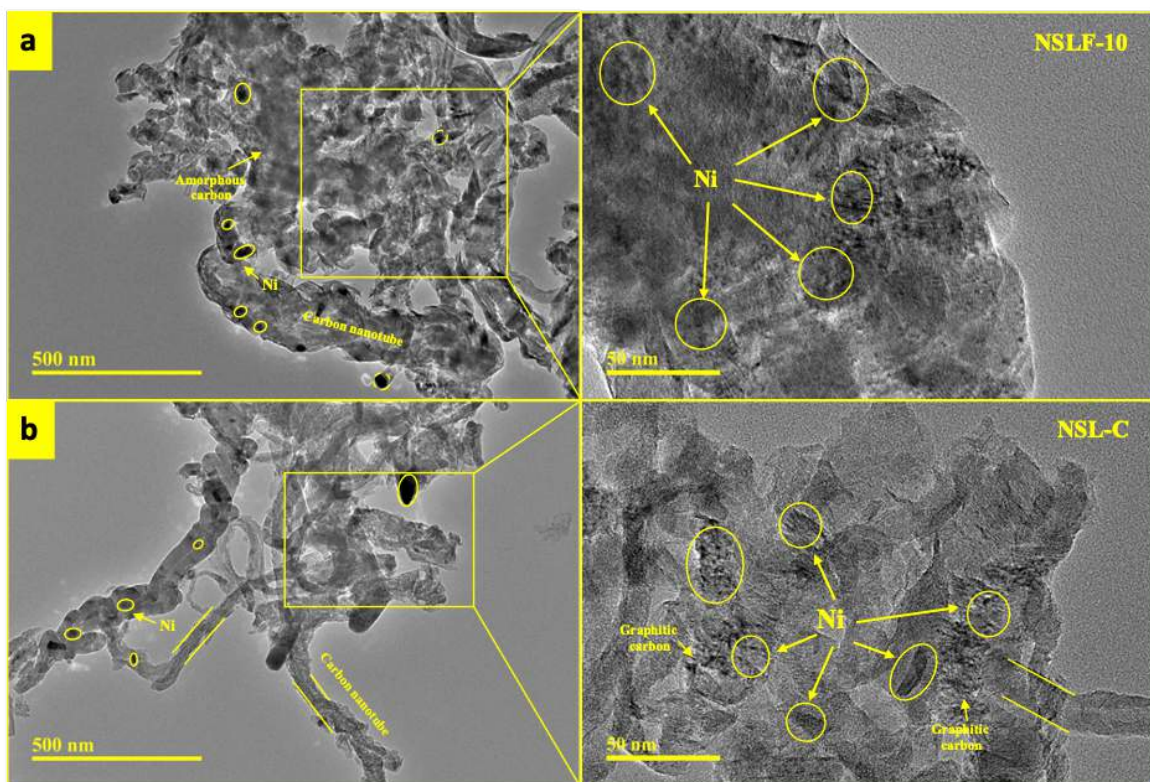


Figure 4.16: TEM images of spent catalysts after 22 h TOS reaction: (a) NSLF-10 catalyst and (b) NSL-C catalyst.

can be attributed to the occurrence of the  $\text{CH}_4$  cracking, which resulted in more  $\text{H}_2$  amount and coke production on the surface of the catalysts as showed by the Raman and TEM.

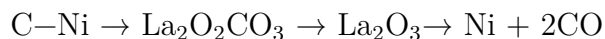
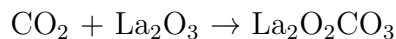
#### 4.2.4 Proposed reaction mechanism

The effect of incorporating 10 wt.% Ni into the core-fibrous shell SLF and composite silica lanthanum oxide catalysts was investigated, and the effects are summarized. In the case of the fibrous structured (SLF) catalyst, Figure 4.17 illustrates the production of Si-O-Ni bonds and the SMSI. The proposed mechanism for the DRM involving NSLF catalysts, particularly focusing on the incorporation of  $\text{La}_2\text{O}_3$ , suggests a bi-functional mechanism despite the presence of inert  $\text{SiO}_2$  support. This mechanism involves intricate interactions where Ni facilitates the dissociation of  $\text{CH}_4$  and  $\text{CO}_2$ , while  $\text{La}_2\text{O}_3$  supplies oxygen species crucial for the WGS reaction and the prevention of coke formation. Additionally,  $\text{La}_2\text{O}_3$  aids in stabilizing Ni particles, thus preventing sintering and maintaining the catalytic activity. The initial step involves methane activation that occurs on the Ni active sites.  $\text{CH}_4$  molecules adsorb on the Ni surface, and the C-H bond is weakened. This process requires a certain activation energy which is provided by the presence of Ni active metal. SLF may also play a significant role in stabilizing the Ni active sites and enhancing their interaction with  $\text{CH}_4$ . This process dissociates  $\text{CH}_4$  on the Ni surface and generates  $\text{CH}_x^*$  and  $\text{H}^*$  species on the Ni surface. Simultaneously, the presence of  $\text{La}_2\text{O}_3$  may facilitate  $\text{CO}_2$  activation by providing  $\text{O}_V$ , which can stabilize  $\text{CO}_2$  adsorption. The activation of  $\text{CO}_2$  facilitates its decomposition into CO due to the support. This activation step is crucial for promoting the subsequent reactions. Notably, the dimensions and dispersion of NiO NPs exhibited extensive variation with alterations inside the supported morphology. The catalytic conversion was attributed to SMSI, increased active sites, NiO distri-

bution, and enhanced basicity attributed to the addition of  $\text{La}_2\text{O}_3$ , which facilitated  $\text{CH}_4$  activation and  $\text{CO}_2$  adsorption [228]. TEM images confirmed that NiO NPs displayed superior dispersion and smaller particle size when loaded onto SLF compared to NSL-C. In NSL-C, NiO was limited, and agglomeration of NiO occurred. The dispersion of NiO performed a vital role in changing the O-Si and O-H of SLF with Ni ions, forming Si-O-Ni bonds. The SMSI found in NSLF-10 played a pivotal role in preserving reduced form of  $\text{Ni}^0$ , supplying abundant active sites, stopping coke deposition, and inhibiting metallic sintering under hard reaction conditions. These factors contributed to the superior catalytic stability and activity of NSLF-10. Conversely, the weak MSI in NSL-C resulted in inadequate Si-O-Ni bond formation, leading to a sizeable amount of coke deposition and excessive sintering due to the larger size of NiO NPs. This defined the relatively poor catalytic performance of NSL-C. The activation of  $\text{CH}_4$  is due to the occurrence of Ni, resulting in the formation of Ni-C and  $2\text{H}_2$ .



The adsorption of  $\text{CO}_2$  and the subsequent formation of a  $\text{La}_2\text{O}_2\text{CO}_3$  intermediate carbonate followed through its reaction with C-Ni to regenerate  $\text{La}_2\text{O}_3$ , Ni, and CO prevented carbon deposition at the catalyst surface.



This intermediate carbonate reacts with carbon atoms on the Ni surface (C-Ni), leading to the regeneration of Ni, CO, and  $\text{La}_2\text{O}_3$ . This regeneration process is essential for sustaining the catalytic activity of the Ni. Nevertheless, the high  $\text{H}_2/\text{CO}$  ratio

observed during stability testing likely arises from  $\text{CH}_4$  decomposition and the limited formation of CO from  $\text{La}_2\text{O}_2\text{CO}_3$ , acting as a coke oxidizing agent, or from the occurrence of the WGS reaction at this high temperature, in which CO reacts to form  $\text{CO}_2$  and  $\text{H}_2$ . This is because most of the  $\text{La}_2\text{O}_3$  is positioned away from the Ni NPs, primarily in the core. Consequently, accumulated  $\text{La}_2\text{O}_2\text{CO}_3$  covers a significant portion of the support during reactions. When a small fraction of  $\text{La}_2\text{O}_3$  is close to Ni NPs, it quickly forms filamentous carbon due to the densely packed distribution of Ni NPs. The build-up of coke and the transition from filamentous to non-filamentous carbon result from an imbalance between filamentous carbon growth and the limited involvement of  $\text{La}_2\text{O}_3$  in carbon removal. The deposition of non-filamentous carbon can cover the active sites of Ni, leading to their deactivation during the process. Overall, NSLF-10 exhibited the highest conversion with stability over 22 h without signs of deactivation, due to its enhanced physicochemical properties and incorporation of  $\text{La}_2\text{O}_3$ .

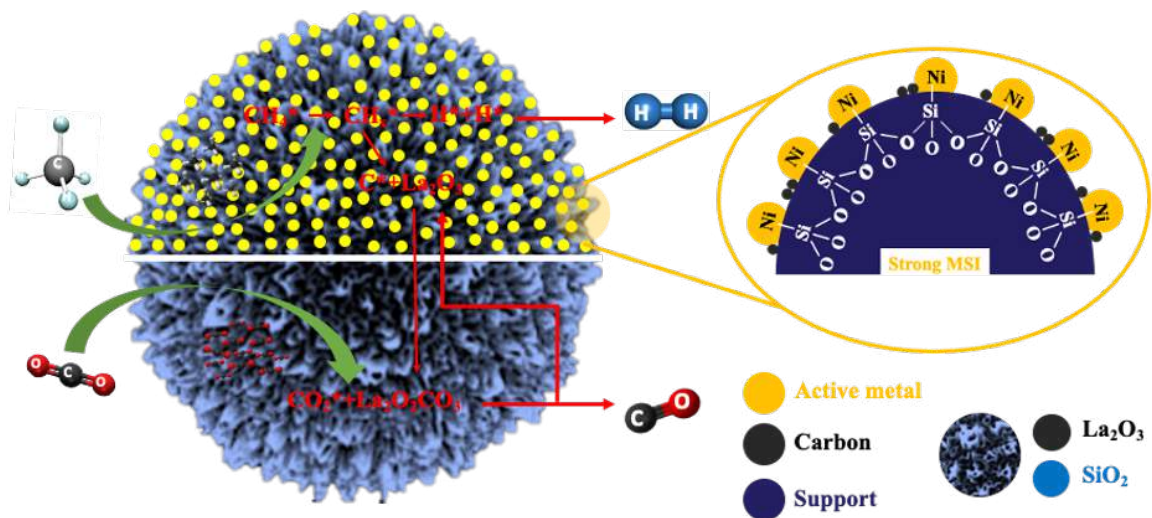


Figure 4.17: Proposed reaction mechanism of NSLF-10 catalyst for the DRM process.

### 4.3 Ni-based Fibrous Silica Lanthanum-Oxide (NSLF) Catalysts

Herein, we have developed a catalytic system for DRM using a mixed metal oxide support (silica-lanthanum oxide; SLF) to support Ni-based catalysts by the utilization of microemulsion and impregnation methods. We aimed to enhance the catalyst's basicity and inhibit carbon formation on  $\text{SiO}_2$  by integrating  $\text{La}_2\text{O}_3$ . To the best of our knowledge, there are no previous reports on the synthesis of SLF support with this specific morphological structure and using this synthesis method for DRM. Our primary objective is to investigate the influence of the morphology and textural properties of the SLF support on nickel active metal and explore the impact of nickel loading on the SLF for DRM. The SLF structure can increase the dispersion of the nickel particles due to the presence of the fibrous shell and the enhanced surface area,

and limit the agglomeration of nickel particles. Therefore, carbon deposition can be limited and the overall performance of DRM can be improved.

#### **4.3.1 Fresh catalysts characterization**

The morphology of the SLF support and active metal plays a crucial role in understanding and correlating the catalytic efficiency with the porosity, size, shape, distribution, and arrangement of various structures in the materials. Therefore, the morphological structures of the produced catalysts were examined using FESEM and TEM. TEM was employed to study the microstructure of the SLF support, as illustrated in Figure 4.18. The TEM micrographs reveal core-fibrous shell structures around well-ordered micro/nanospheres supported by  $\text{SiO}_2$  fibers in all axial orientations, as shown in Figure 4.18(a,b). An interconnected network of porous and dimensional nanofibers was visible in the TEM images of the 500–100 nm SLF support. The TEM image of the 200 nm NSLF-8 catalyst (Figure 4.18c) depicts a similar fibrous structure, but the SLF is coated with evenly distributed Ni species with an average particle size of 19 nm NiO. The nanofibers appeared to be finer and more tightly packed, potentially leading to an even greater surface area and enhanced porosity, as observed in Figure 4.18d. The TEM images in Figure 4.18(e, f) demonstrate the presence of La, Si, and Ni in the fibrous matrix.

Furthermore, Figure 4.19 depicts the FESEM images of the NSLF-x catalysts. The FESEM micrographs revealed a connected system of porous nanoscale fibers, contributing to the material's extensive surface area and potential porosity due to variations in fiber length and diameter. Notably, there was no indication of particle ac-

cumulation in NSLF-6, NSLF-8, NSLF-11, and NSLF-15. The growth of a core-fibrous shell morphology involves  $\text{SiO}_2$  species forming the fibers of the shell. Significantly, a noticeable variation in inter-fiber distance enhances the textural characteristics of the developed catalyst, potentially augmenting the mesoporosity and SLF surface area. The surface of the SLF support appeared predominantly smooth with only a few rough edges. FESEM images of NSLF-x catalysts with various Ni quantities are presented also in Figure 4.20(b-f). Overall, all catalysts exhibited practically identical morphology when Ni was added to SLF, maintaining its spherical shapes. The elemental distributions of the NSLF-x catalysts were explored by FESEM-EDS mapping, as depicted in Figure 4.20. Figure 4.20(b-e) illustrates the uniform distribution of La, O, Si, and Ni elements in the samples. This demonstrates how different Ni loadings on SLF resulted in diverse dispersions of NiO NPs within the  $\text{SiO}_2$  fibrous network. The SLF is expected to increase MSI by preventing the NiO crystal from agglomerating and by enhancing the active site mobility for NiO dispersion. Also, the SEM-EDS mapping of the samples revealed the spatial distribution of these elements, shedding light on their structure within the fibrous  $\text{SiO}_2$  network. A homogeneous distribution of small NiO crystallites in well-separated dispersion can be observed in all samples. La distribution was observed on the fibrous  $\text{SiO}_2$  surface, providing crucial details on its spatial arrangement within the support. Moreover, the SEM-EDS spectrum exhibited typical peaks corresponding to the components present in the sample, as shown in Figure 4.21. Significant peaks for Si, La, O, and Ni were identified, confirming the presence of these elements in the fibrous structure. The magnitude and position of these peaks provided quantitative data on the relative abundance of the

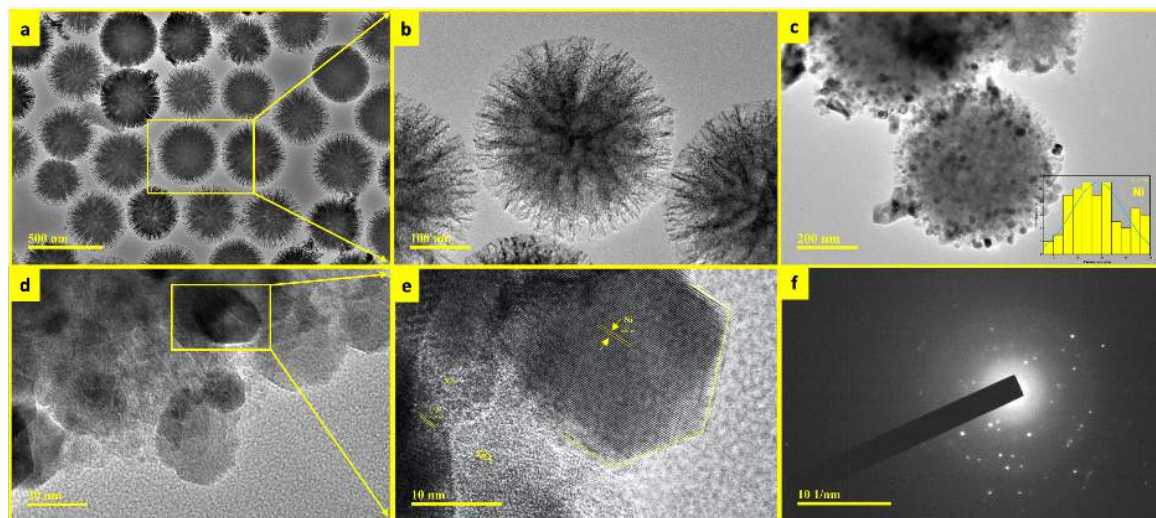


Figure 4.18: TEM images of (a, b) SLF support, (c, d, e) NSLF-8 catalyst; and (f) Saed pattern of NSLF-8 catalyst.

catalyst. The distribution of all elements is uniform, and the contents of the elements closely match those of the synthesis. This suggests that both the microemulsion and wet impregnation methods can effectively yield catalysts with uniformly distributed active elements.

$N_2$  adsorption-desorption isotherms and pore size distribution analyses were utilized to examine the textural characteristics of the produced catalytic materials. The specific surface areas, pore volumes, and pore diameters for SLF and SLF loaded with Ni are summarized in Table 4.4, and  $N_2$  adsorption-desorption isotherms are depicted in Figure 4.22. A type IV isotherm with the presence of the hysteresis loop was observed, indicating capillary condensation at  $P/P^o$  values of 0.3 and 0.9, which signifies the presence of intraparticle and interparticle voids in the SLF mesoporous structure. Hysteresis loops observed in the case of SLF suggested effective mesopore formation. Additionally, the reduction in  $N_2$  adsorption observed when NiO existed on SLF proposed that NiO particles were being deposited onto the SLF. The pore size

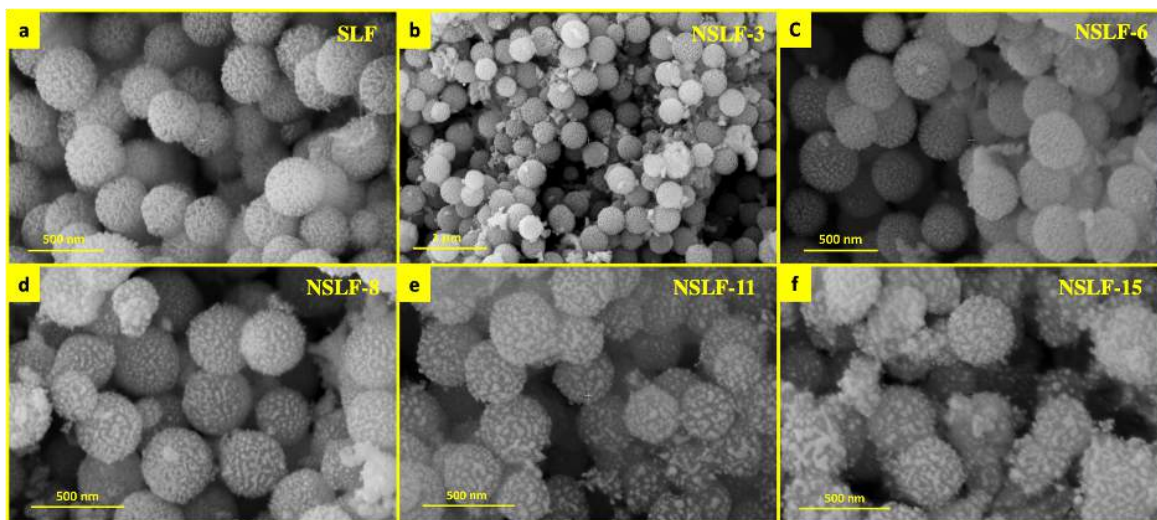


Figure 4.19: SEM images of the fresh NSLF- catalysts.

distribution for each catalyst was determined as presented in Figure 4.22. The smaller peaks were attributed to fibrous molecule spacing, while the larger peak was caused by mesopores created by surfactant self-assembly. SEM images in Figure 4.22(b-f) showed that Ni was dispersed with microscopic size, and there was no discernible change in pore distribution between NSLF and SLF. Both SLF and Ni-doped SLF exhibited intrinsic mesoporosity due to induced fibrosis, resulting in significantly larger pore volume and specific surface area. This larger surface area facilitated a wider dispersion of active metal particles. Furthermore, the increased Ni on the SLF surface suggested effective metal distribution. Due to the SLF fibrous form, which provided numerous active sites for NiO dispersion, there was less chance of high MSI and NiO crystal agglomeration. The fibrous shape of SLF enabled improved accessibility and distribution of Ni through its 3D hierarchical channel, as observed in a previous study [229].

XRD analysis was employed to determine the crystallinity and structure of the

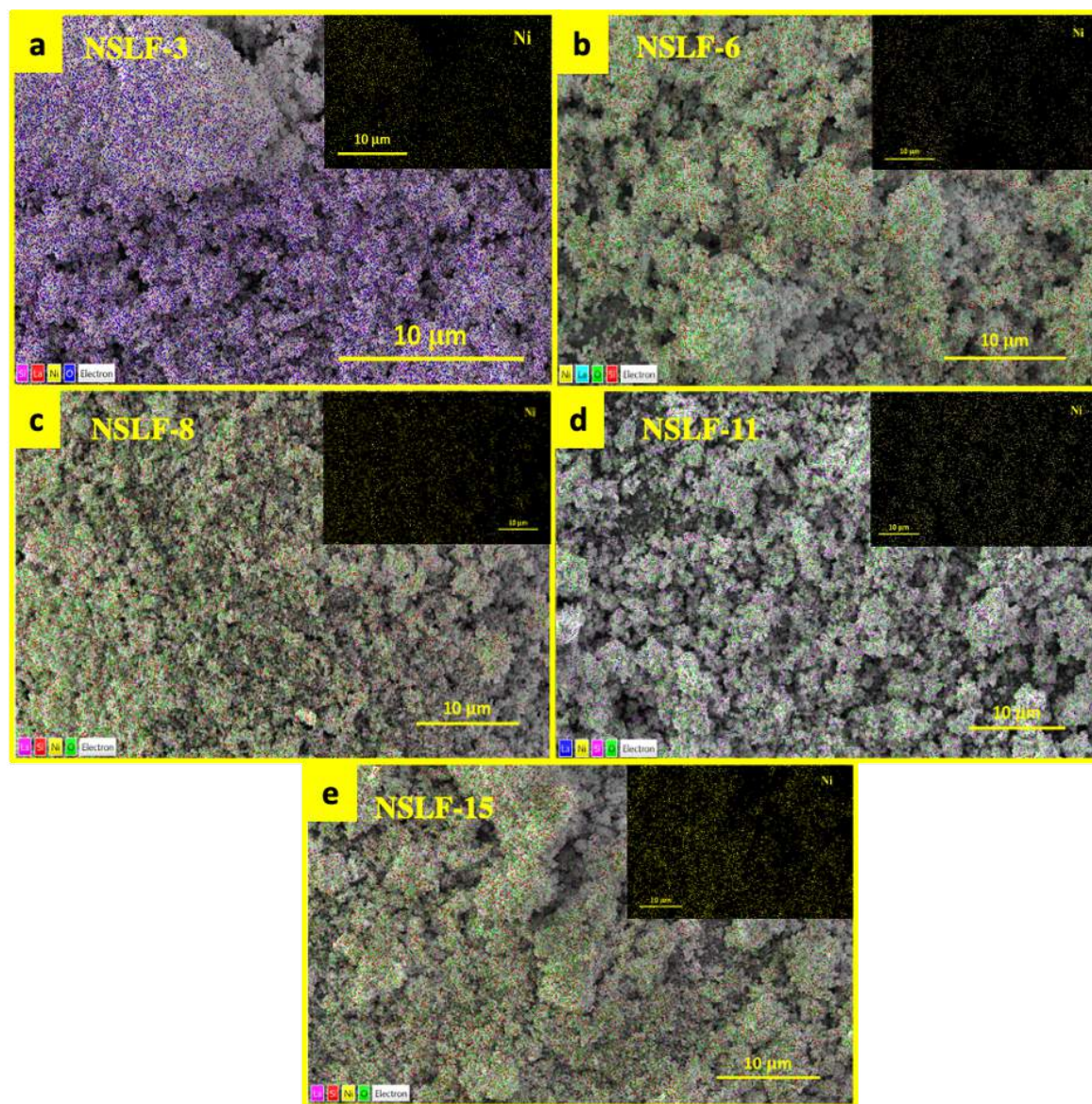


Figure 4.20: The FESEM-EDS mapping of the fresh NSLF-x catalysts.

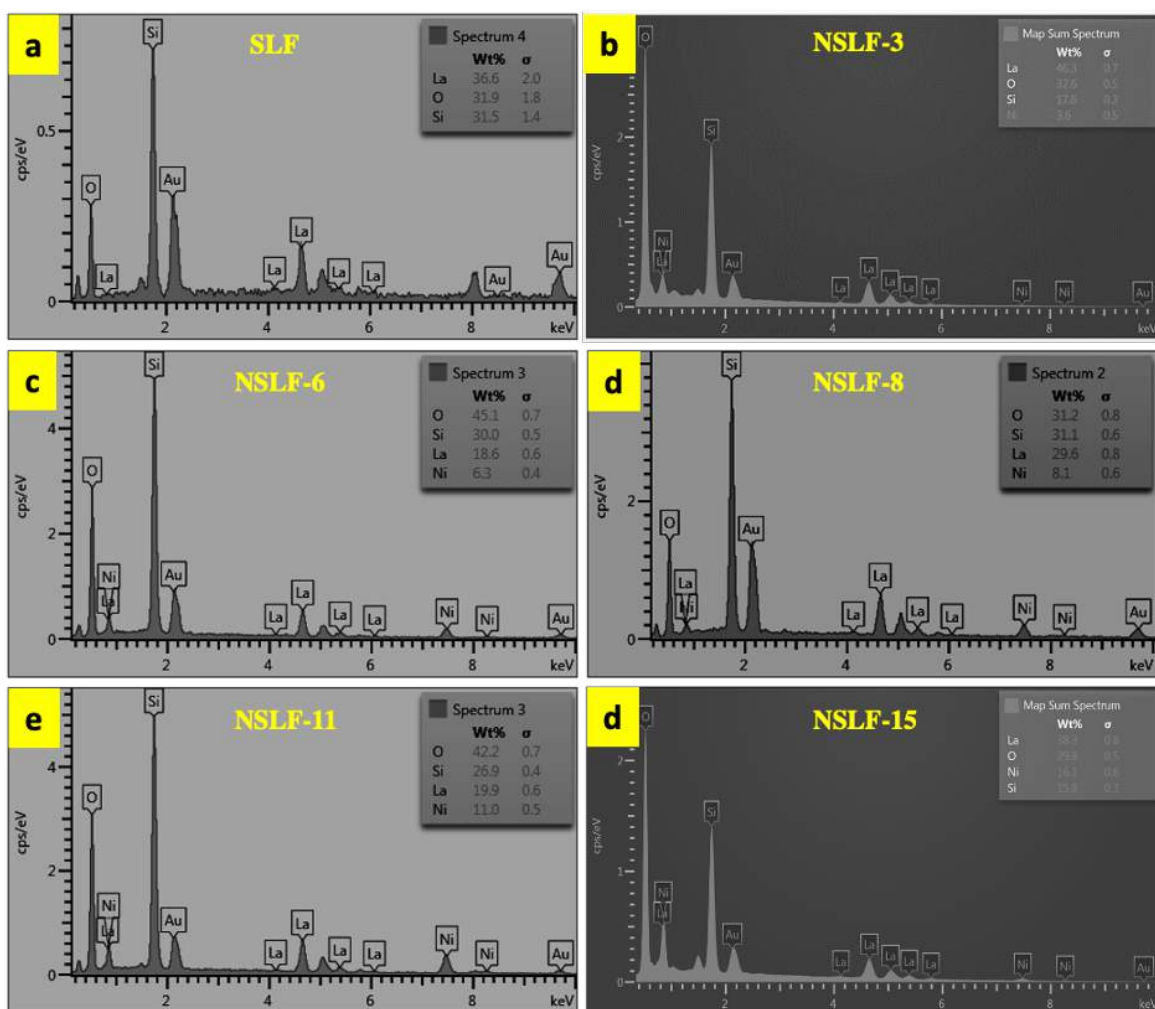


Figure 4.21: The FESEM-EDS spectrum of the fresh NSLF-x catalysts.

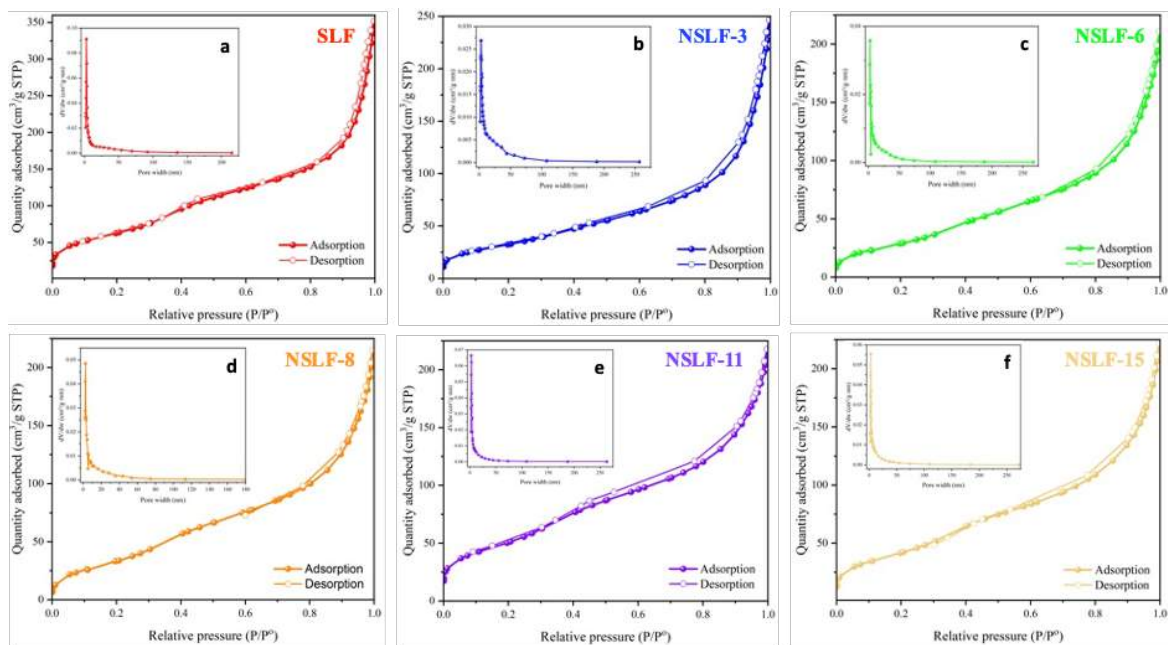


Figure 4.22: N<sub>2</sub> adsorption-desorption isotherms and the pore size distributions of the fresh catalysts.

catalysts. Figure 4.23a depicts the XRD patterns of NSLF-x catalysts, which include diffraction peaks in the 20-80° range. Peaks at angles of 20.7°, 21.5°, 24.3°, 26.9°, 31.1° and 32.1° are frequently attributed to the SiO<sub>2</sub> texture (COD card No. 00-400-2433). Additionally, five strong and dominant peaks at 26.1°, 30.0°, 46.1°, 55.4° and 72.08° (COD card No. 00-200-2286) were found to correlate to the (100), (101), (102), (2-10), (004), (201) and (203) La<sub>2</sub>O<sub>3</sub> crystalline layers. Additionally, the peaks at 37.2°, 43.4°, and 62.7° following NiO impregnation correlate to (111), (200), and (220), respectively, and match with COD card No. 00-432-0508. For Ni loadings ranging from 3 to 15 wt.%, diffraction intensities evolved in the following order: NSLF-3, NSLF-6, NSLF-8, NSLF-11, and NSLF-15. Figure 4.23a also displays very high NSLF-15 NiO peak concentrations. The SEM images verified that the NSLF-6, NSLF-8, NSLF-11, and NSLF-15 showed no accumulation due to fine dispersion and inclusion.

| Catalysts | Ni content (%) <sup>a</sup> | Surface area (m <sup>2</sup> /g) <sup>b</sup> | Total pore volume (cm <sup>3</sup> /g) | Pore size (nm) | Ni crystallite size (nm) <sup>c</sup> |
|-----------|-----------------------------|-----------------------------------------------|----------------------------------------|----------------|---------------------------------------|
| SZL       | -                           | 362.3                                         | 0.412                                  | 4.549          | -                                     |
| NSLF-3    | 3.6                         | 140.0                                         | 0.249                                  | 8.284          | 24.53                                 |
| NSLF-6    | 6.3                         | 160.1                                         | 0.228                                  | 8.299          | 21.88                                 |
| NSLF-8    | 8.1                         | 194.4                                         | 0.307                                  | 7.463          | 19.08                                 |
| NSLF-11   | 11                          | 189.6                                         | 0.261                                  | 5.615          | 16.80                                 |
| NSLF-15   | 15.8                        | 187.5                                         | 0.248                                  | 6.368          | 14.63                                 |

<sup>a</sup> Determine from the EDS

<sup>b</sup> Determine from the BET and BJH

<sup>c</sup> Determine from the Scherrer equation

Table 4.4: Textural properties of the synthesized NSZF catalysts.

In addition, Figure 4.23b shows the structural changes and functional groups in the Ni supported on SLF by FTIR spectroscopy. The notable peaks were observed between 400 and 1400 cm<sup>-1</sup> point to the existence of Si in several interactions, such as Si–O, Si–O–Si, Si–O–La, and La–O [230], which appearing at 1090.5, 807.9, and 470.2 cm<sup>-1</sup>. Both SLF support and NSLF-x catalysts exhibited distinct transmittance maxima of Si–O–Si materials in the 1000–1300 cm<sup>-1</sup> range. Likewise, the major transmittance maxima at about 1090.5 cm<sup>-1</sup> and 807.9 cm<sup>-1</sup>, respectively, were associated with the longitudinal-optical (LO) and transverse-optical (TO) asymmetrical stretching bands of Si–O–Si [231]. At 470 cm<sup>-1</sup>, the La–O stretch vibrational was found [232]. Similarly, the peaks observed at 1090.5 cm<sup>-1</sup>, 807.9 cm<sup>-1</sup>, and 470 cm<sup>-1</sup> were recognized to Si–O–La stretching vibrations as well as symmetrical and asymmetric stretching vibrations. The La–OH framework was identified by the band at 3442 cm<sup>-1</sup>. The strong peak observed at 970 cm<sup>-1</sup> in NSLF-x catalysts is likely associated with the interaction between transition metal atoms and the surrounding siliceous material framework. This interaction specifically involves the Si–O stretching vibrations, which play a significant role in the observed structure [233]. The presence of nickel

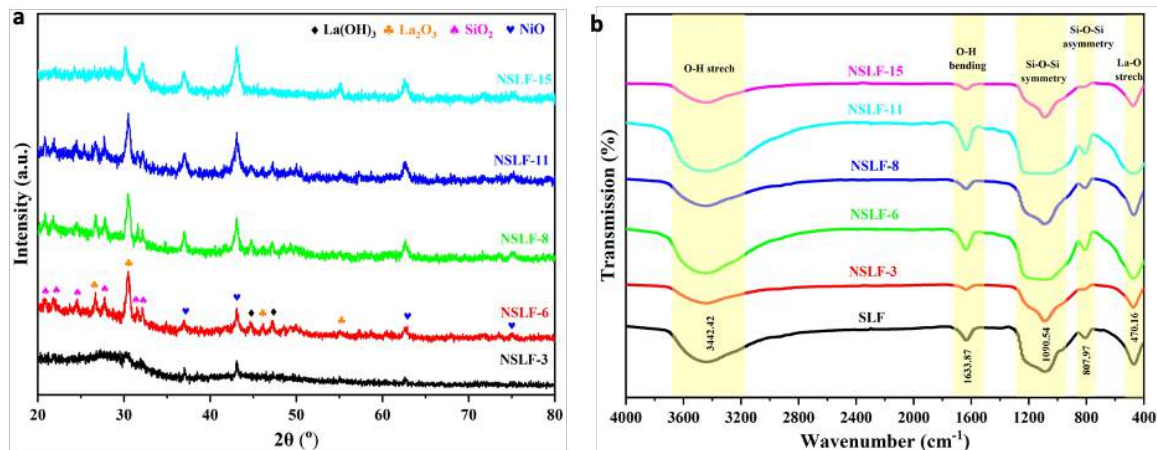


Figure 4.23: (a) XRD patterns of the fresh NSLF-x catalysts, and (b) FTIR spectra of NSLF-x catalysts.

particles on SLF results in the growth of Si–O–Ni bonds, potentially causing a shift in the band and a reconfiguration of the Si–OH group surfaces. The presence of –OH groups is visible in the 2500–3700  $\text{cm}^{-1}$  FTIR spectra, and their interaction is particularly noticeable in the peak at 3400  $\text{cm}^{-1}$  [234], as shown in Figure 4.23b. It may be concluded from this result that SLF was effective in forming a strong Si–O bond with oxygen atoms and –OH molecules. This is explained by the fact that SLF contains the siliceous fibrous component, which considerably aids in the production of terminal silanol groups. After nickel doping on the supports, specific bands’ intensities, notably those at 1090.5  $\text{cm}^{-1}$  and 807.9  $\text{cm}^{-1}$ , showed appreciable drops as compared to the untreated support. As previously mentioned, the presence of 961  $\text{cm}^{-1}$  band denotes the active metal ions integration onto the meso-silica and formation of Si–O–Ni bonds [235].

The surface properties of NSLF-x catalysts and the reducibility of nickel species were investigated using the  $\text{H}_2$ -TPR analysis, as shown in Figure 4.24a. In general, the reduction peaks observed at lower temperatures, ranging from 300 °C to 500 °C,

are indicative of the reduction of NiO to metallic nickel species that exist on the catalytic surface. Conversely, the observed peak within this range can be attributed to the reduction of Ni, which interacts with the support. A noticeable decline peak with various heights can be observed in H<sub>2</sub>-TPR profiles for all samples, coupled with a peak that occurs at temperatures higher than 600 °C except NSLF-3. The decrease in peak intensity can be attributed to the presence of nickel species with varying sizes, natures, and strengths of MSI. The peak observed at 350 °C corresponds to the reduction of smaller-sized NiO or surface-bound NiO, while the peak ranging from above 350 °C to 510 °C relates to the NiO reduction [236]. The lowest concentration of bulk NiO is confirmed by the disappearance of the high-temperature peak in the case of NSLF-8, which is consistent with the scattering of particle sizes shown in SEM [237]. However, a peak that appears at a lower reduction temperature may indicate that there is little interaction between the surface NiO species and the exterior SLF fibers, as in the case of NSLF-3 [238]. The reduction peaks in the catalysts moved towards higher temperatures as the amount of Ni in the catalyst increased, indicating the existence of SMSI between Ni and La species. The presence of La in the support enhances electron transfer from La<sup>3+</sup> to Ni<sup>2+</sup>, resulting in higher electron density at Ni 3d orbitals because of La<sup>3+</sup> reduced electronegativity. The increased contact between Ni and the support boosts the reduction temperature [233]. Obviously, the peak for NSLF-15 was significantly higher and broader than the other catalysts, suggesting better NiO reduction. Moreover, NSLF-11 and NSLF-15 exhibited a significant peak centered around 600 °C, with the largest peak area. These findings suggest an increased abundance of Ni particles, indicating a SMSI, smaller and more evenly dis-

tributed Ni particles, as evidenced by the SEM images, and a higher concentration of reducible NiO. These observations align with the catalytic performance, particularly NSLF-15, which demonstrated enhanced catalytic stability and activity.

Moreover, CO<sub>2</sub>-TPD was conducted to investigate the adsorption capacities of CO<sub>2</sub> and the surface alkalinity of the catalysts. It is worth noting that a prominent broad peak was observed for all catalysts, indicating the presence of basicity in the catalysts, as depicted in Figure 4.24b. Desorption peaks below 200 °C are typically indicative of weakly basic sites, resulting from the physical adsorption of the samples and the existence of hydroxyl groups (–OH). On the other hand, peaks within the temperature range of 200 to 500 °C correspond to moderately basic sites, which can be recognized as the existence of metal-oxygen ion pairs on the sample surface. Strongly basic sites, typically linked to O<sub>V</sub> sites and low-coordinated oxygen sites, are indicated by peaks above 500 °C. The presence of broad peaks spanning from 75 °C to 280 °C suggests the existence of varying degrees of weak and moderate basicity across all samples. As La<sub>2</sub>O<sub>3</sub> exhibits the ability to absorb a significant amount of CO<sub>2</sub>, forming La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, and decomposes above 500 °C, the catalysts display small peaks around 623 °C, confirming the presence of the La<sub>2</sub>O<sub>3</sub> phase in these catalysts (Figure 4.24b) [239]. Hence, it is significant to highlight that the NSLF-15 catalyst exhibited a notably high intensity of CO<sub>2</sub>-TPD signals, indicating a boosted concentration of weak and moderated basic sites, along with a proportion of strong basic sites. Therefore, it can be concluded that NSLF-15 possessed both weak, moderate, and strong basic sites.

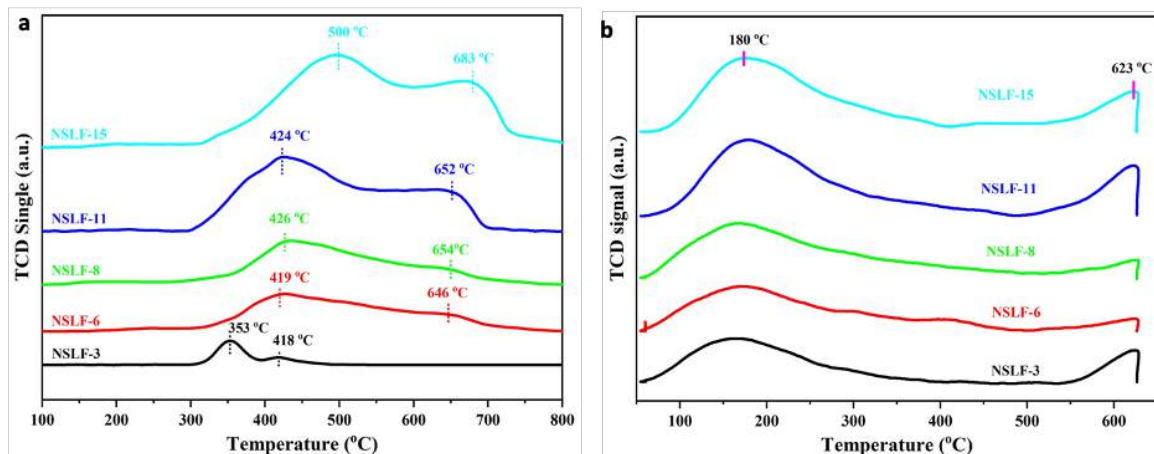


Figure 4.24: (a) H<sub>2</sub>-TPR profile of the fresh catalysts, (b) CO<sub>2</sub>-TPD profile of the fresh catalysts.

### 4.3.2 Catalytic performance

The catalytic activity of the NSLF-x catalysts was investigated by determining the conversion of reactants, the yield of products, and H<sub>2</sub>/CO ratio under the different reaction temperatures, as shown in Figure 4.25. The concept of DRM, which highlights the necessity of both support and metal activity to achieve desirable catalytic performance, has already been described in the literature [240][241]. It has been observed that the selection and optimization of catalytic properties are crucial for achieving efficient and sustainable DRM processes in various applications. Therefore, we investigated the conversion of CH<sub>4</sub> and CO<sub>2</sub> with different Ni loadings. This property of catalysts plays a significant role in determining their efficiency in facilitating chemical reactions. Figure 4.25(a,b) displays the CO<sub>2</sub> and CH<sub>4</sub> conversion that were determined throughout a temperature range of 500 to 1000 °C. Interestingly, increasing the Ni content (as in the case of NSLF-15) enhances the conversions significantly due to the uniform dispersion of Ni species on the support. This will produce a large number of

active sites of metallic NiO, which facilitates the mass transfer of gaseous CH<sub>4</sub>/CO<sub>2</sub> within the catalyst. In terms of CH<sub>4</sub> conversion, the NSLF-6 catalyst achieved a conversion of 20% at 550 °C, whereas the NSLF-8 catalyst demonstrated a higher conversion of 35% under the same conditions. However, the NSLF-11 catalysts exhibited a slight decrease in CH<sub>4</sub> conversion at the same temperature due to carbon formation on the catalytic active sites. The same trend was observed for CO<sub>2</sub> conversion. It has been observed that the conversion of CH<sub>4</sub> was higher than that of CO<sub>2</sub>, which can be attributed to side reactions such as the Boudouard reaction and CH<sub>4</sub> decomposition. As demonstrated in Figure 4.25(a,b), raising the temperature from 650 to 900 °C enhanced the CO<sub>2</sub> and CH<sub>4</sub> conversions for all catalysts, in which the NSLF-8, NSLF-11, and NSLF-15 achieved a conversion of almost 99%. This is because of increased Ni content in the catalyst, indicating the existence of SMSI between Ni and lanthanum species. The presence of lanthanum in the support enhances electron transfer from La<sup>3+</sup> to Ni<sup>2+</sup> and thus increases the contact between Ni and the support, suggesting a higher concentration of reducible NiO. All these observations align with the catalytic performance, particularly NSLF-15, which demonstrated enhanced catalytic stability and activity. The H<sub>2</sub>/CO ratio displayed in Figure 4.25f was used to predict the coexistent secondary reactions that occurred during the catalytic evaluation. The increase in the syngas ratio can be primarily attributed to two processes. Firstly, the Boudouard reaction arises at temperatures below 650 °C, leading to the production of carbon (C) and CO<sub>2</sub>. Secondly, the decomposition of CH<sub>4</sub> takes place at temperatures above 650 °C, resulting in the formation of C and H<sub>2</sub>. These processes contribute to the higher syngas ratio observed in the catalyst system [242]. Moreover,

the formation of carbonaceous species through secondary reactions negatively impacts catalytic performance. Additionally, the RWGS reaction contributes to a drop in the syngas ratio. Thermodynamic predictions suggest that this reaction becomes more pronounced at higher reaction temperatures. This is because the produced  $H_2$  is consumed in the reduction of  $CO_2$  to  $CO$ , resulting in a reduction in the overall syngas ratio, as observed in the case of NSLF-3 [243]. At reaction temperatures below 700 °C, the experimental results demonstrated that the molar ratio of  $H_2/CO$  approached unity, aligning with the desired outcome of an optimal DRM reaction. However, for all the tested catalysts at higher reaction temperatures, the molar ratio of  $H_2/CO$  exceeded 1, except NSLF-3. This indicates that the decomposition of  $CH_4$  side reaction occurred, leading to the production of a higher amount of  $H_2$  and causing an increase in the  $H_2/CO$  ratio as well as  $H_2$  yield, as depicted in Figure 4.25(c, e). Consequently, the  $CO$  yield was reduced, as shown in Figure 4.26 [244]. The measured  $H_2$  yield for the different samples at a temperature of 800 °C followed the order: NSLF-15 (80%) > NSLF-8 (77%) > NSLF-11 (74%) > NSLF-6 (51%) > NSLF-3. Therefore, among the tested catalysts, the NSLF-15 catalyst demonstrated the most exceptional performance within the temperature range of 750 to 1000 °C. In contrast, the significantly low efficiency observed for the NSLF-3 catalyst indicates a limitation in the development of weak/medium MSI. The inadequate presence of active Ni metals in the NSLF-3 catalyst hinders its ability to effectively promote catalytic performance, which reduces the overall efficiency of the catalyst. The differences in catalytic efficiency observed among the catalysts can be attributed to the strength of the activated metallic NiO species that are formed through the synergistic combination of NiO and

the SLF framework.

Furthermore, the catalytic stability was evaluated for 28-h TOS at 750 °C, as depicted in Figure 4.27. The catalysts displayed remarkable stability throughout the reaction time, with no indications of deactivation, except for NSLF-6 and NSLF-11. The conversions showed an increasing trend with higher Ni loading up to 15 wt.%, but a significant decrease was observed for the NSLF-3 (3 wt.% Ni). This difference can be attributed to the varying number of accessible active sites on the catalyst surface due to different Ni loadings. However, the NSLF-15 catalyst exhibited excellent performance, suggesting that 15 wt.% Ni loading is the optimal loading quantity. However, although NSLF-11 catalyst achieved high CH<sub>4</sub> conversions, and smaller CO<sub>2</sub> conversions,. This can be attributed to the catalysts' preference for CH<sub>4</sub> dissociation and weak adsorption of CO<sub>2</sub>. In contrast, NSLF-3, NSLF-6, and NSLF-8 catalysts demonstrated high CO<sub>2</sub> conversions for the first 14 h of the reaction, likely attributable to the favorable CO<sub>2</sub> adsorption provided by the SLF support, as well as the limited CH<sub>4</sub> dissociation and activation by the catalysts. Additionally, the presence of basic sites due to the incorporation of La<sub>2</sub>O<sub>3</sub> in the framework can enhance CO<sub>2</sub> adsorption, as illustrated by CO<sub>2</sub>-TPD. Also, the larger size of Ni particles and poor dispersion of NSLF-3, NSLF-6, and NSLF-8 catalysts result in fewer exposed active sites compared to other catalysts, which is illustrated in Figure 4.19 and Table 4.4 and leads to lower CH<sub>4</sub> conversion. On the other hand, NSLF-6 and NSLF-11 catalysts exhibited a continuous decline in reactant conversion due to carbon formation on the catalytic active sites. In NSLF-11 and NSLF-15, the conversion of CH<sub>4</sub> was higher than that of CO<sub>2</sub>, which can be attributed to side reactions such as the Boudouard reaction

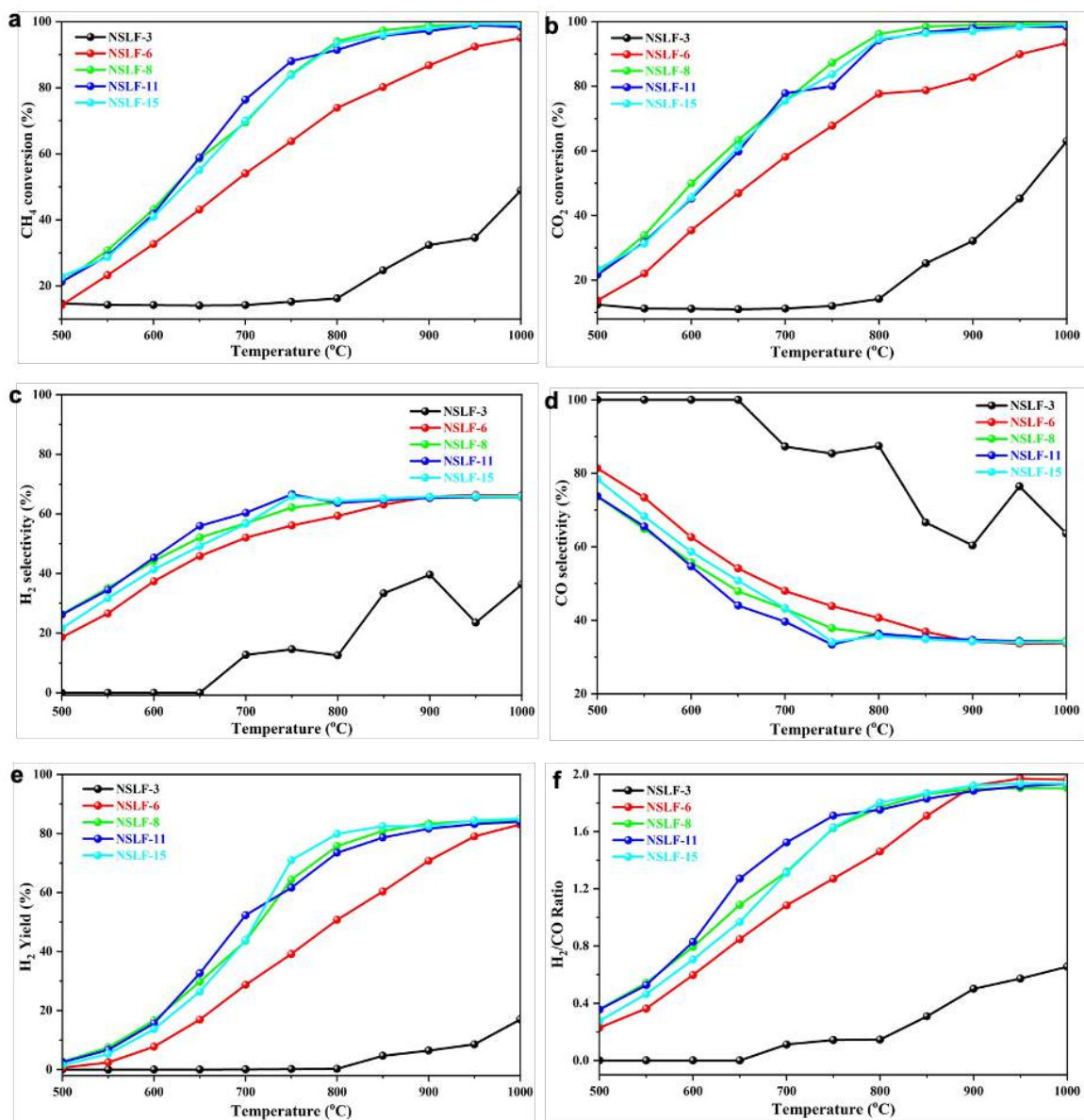


Figure 4.25: Catalytic activity of NSLF-x catalysts: (a) CH<sub>4</sub> conversion, (b) CO<sub>2</sub> conversion, (c) H<sub>2</sub> selectivity, (d) CO selectivity, (e) H<sub>2</sub> yield, and (f) H<sub>2</sub>/CO ratio.

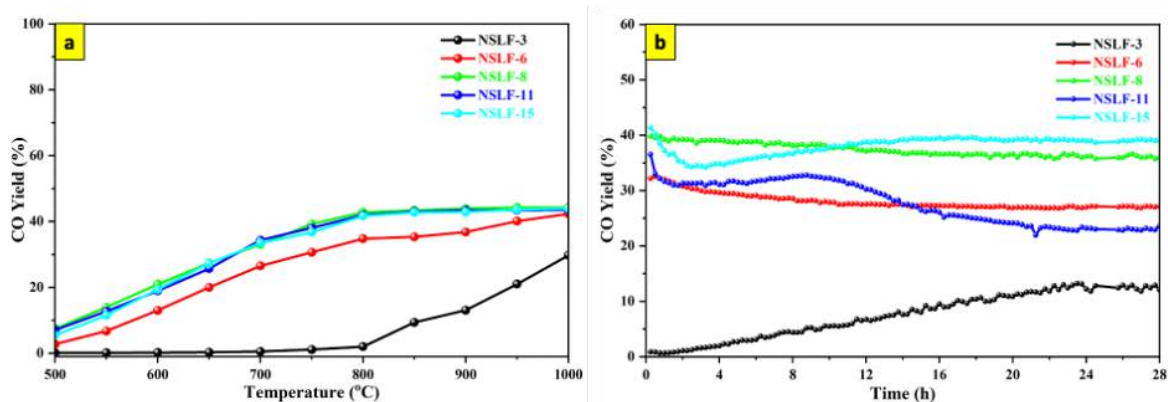


Figure 4.26: (a) CO yield of NSLF-x catalysts during the activity test under different reaction temperature, and (b) CO yield of NSLF-x catalysts during the stability test for 28 h at atmospheric pressure (GHSV=12000 mLg<sup>-1</sup><sub>cat</sub>.h<sup>-1</sup> and CH<sub>4</sub>:CO<sub>2</sub>=1).

and CH<sub>4</sub> decomposition. These reactions not only produce carbon but also enhance hydrogen production and reduce CO production. The formation of coke as a result of these side reactions is the main cause of catalyst deactivation. Additionally, the feasibility of the WGR at elevated temperatures likely contributes to increased H<sub>2</sub> production and decreased CO<sub>2</sub> conversion. The highest conversion was achieved by the NSLF-15 catalyst, reaching 87% for CH<sub>4</sub> and 86.7% for CO<sub>2</sub> under the same conditions. These catalysts exhibited high selectivity and yield towards H<sub>2</sub> rather than CO, as shown in Figure 4.27(c-d). The H<sub>2</sub>/CO ratio for all catalysts (except NSLF-3) was slightly higher than unity (H<sub>2</sub>/CO > 1), corresponding to CH<sub>4</sub> and CO<sub>2</sub> conversions, which has reported in the literature [245][246]. NSLF-3 exhibited a low H<sub>2</sub>/CO ratio due to the occurrence of the RWGS reaction. The observed oscillating patterns in the H<sub>2</sub>/CO ratio for the catalysts can be attributed to the effect of carbon formation and elimination during the reaction [247]. The difference in CH<sub>4</sub> conversion among the catalysts can be attributed to variations in coke behavior, which occurs on the surfaces of Ni particles [248], and is directly linked to the different degrees of

Ni dispersion on the catalysts. Table 4.5 compares the catalytic performance of the NSLF-15 catalysts with those reported in the literature, based on  $\text{SiO}_2$  and  $\text{La}_2\text{O}_3$ .

| Catalysts                                | Temperature | $\text{CH}_4$ conversion (%) | $\text{CO}_2$ conversion (%) | $\text{H}_2/\text{CO}$ Ratio | Ref.      |
|------------------------------------------|-------------|------------------------------|------------------------------|------------------------------|-----------|
| NSLF-15                                  | T=750 °C    | 87                           | 86.7                         | 1.6                          | This work |
| Ni- $\text{La}_2\text{O}_3/\text{SiO}_2$ | T=700 °C    | 77                           | 78                           | 0.98                         | [249]     |
| Ni- $\text{La}_2\text{O}_3/\text{SiO}_2$ | T=700 °C    | 80                           | 85                           | 0.85                         | [250]     |
| Ni@ $\text{SiO}_2$                       | T=750 °C    | -                            | -                            | 1.05                         | [251]     |
| $\text{SiO}_2$ @Ni@ $\text{ZrO}_2$       | T=700 °C    | 43.1                         | 48.8                         | 0.76                         | [252]     |
| Ni/ $\text{La}_2\text{O}_3$ -LOC         | T=700 °C    | 70                           | 75                           | 0.87                         | [253]     |

Table 4.5: Comparison of recently synthesized catalysts based on Ni/ $\text{La}_2\text{O}_3$  and Ni/ $\text{SiO}_2$  for the DRM reaction.

### 4.3.3 Spent catalysts characterization

A comprehensive study of the spent catalysts was conducted using morphological, spectral, and physical analyses after the reaction. The catalytic efficiency in the DRM could be demonstrated by quantifying the formation of coke on the catalysts' surfaces. Various forms of carbon, including amorphous, graphitic, and filamentous carbons, were recognized during the reaction. SEM images of the spent samples, as depicted in Figure 4.28, reveal the formation of filamentous carbon in the spent samples, except for NSLF-3, which exhibits slight the presence of accumulated amorphous carbon clusters, which completely encase the Ni particles with no morphological changes. Figure 4.29 shows TEM images of the spent catalysts collected after 28 h TOS. These images provide evidence of larger Ni particles resulting from Ni agglomeration caused by high-temperature sintering. Furthermore, the growth of filamentous carbon led to the displacement of several Ni particles from the supporting catalyst (SLF). Interestingly,

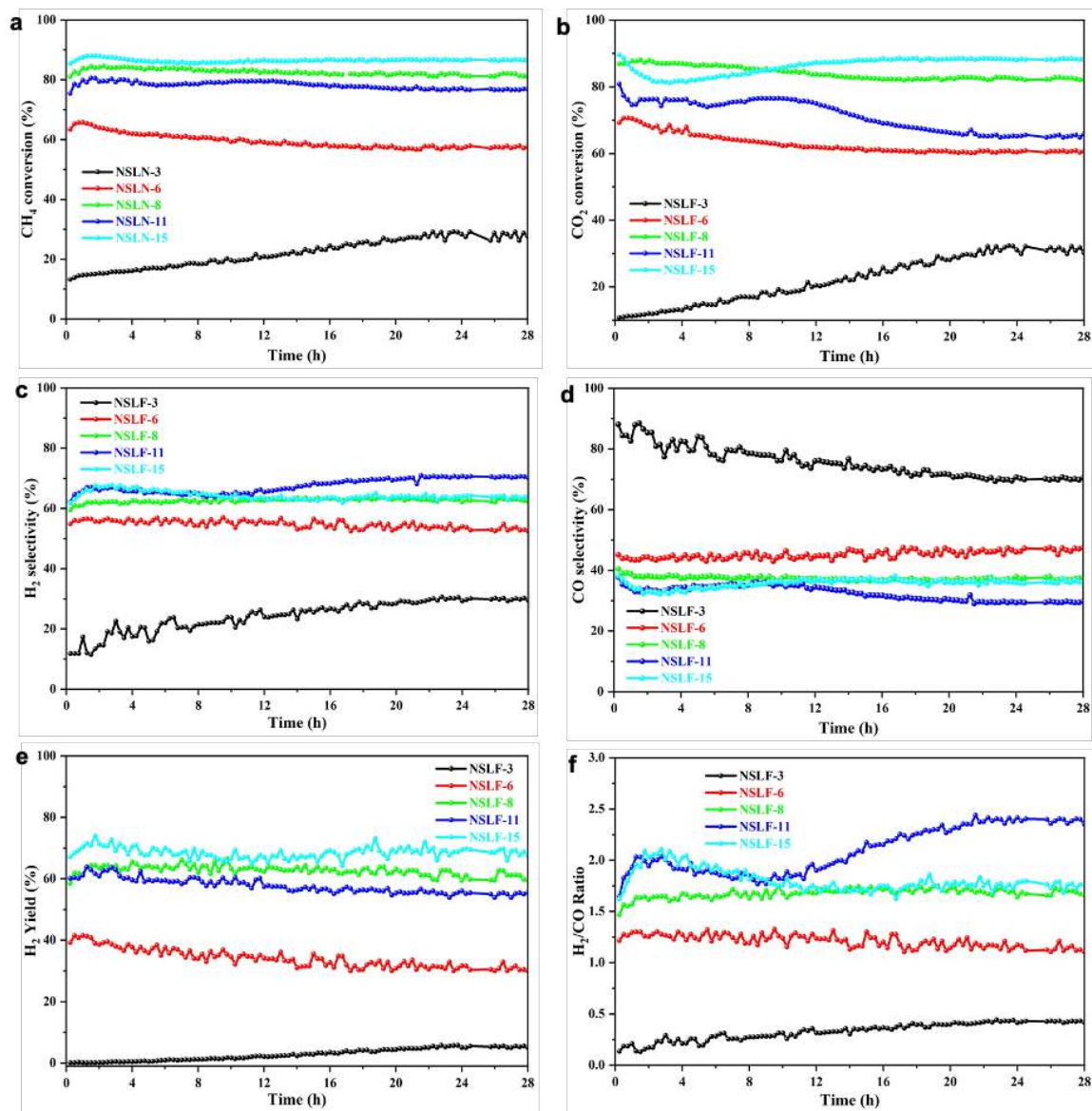


Figure 4.27: Catalytic stability of NSLF-x catalysts: (a) CH<sub>4</sub> conversion, (b) CO<sub>2</sub> conversion, (c) H<sub>2</sub> selectivity, (d) CO selectivity, (e) H<sub>2</sub> yield, and (f) H<sub>2</sub>/CO ratio (conditions: P=1 atm, T=750 °C, GHSV=12000 mLg<sup>-1</sup>cat.h<sup>-1</sup>, t=28 h).

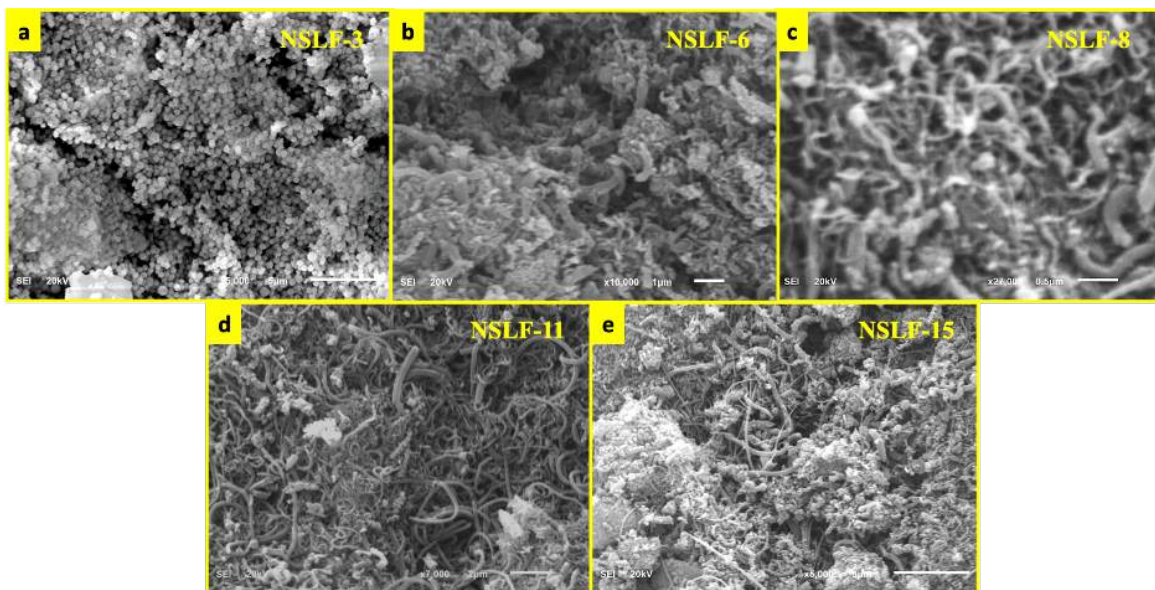


Figure 4.28: SEM images of the spent catalysts after 28 h DRM reaction period; (a) NSLF-3, (b) NSLF-6, (c) NSLF-8, (d) NSLF-11, (e) NSLF-15.

some Ni particles can be observed positioned at the ends of the filaments, serving as evidence of the positive impact of filamentous carbon on Ni dispersion. Despite an increase in the average size of Ni particles when compared to the fresh catalysts, this observation highlights the remarkable resilience of the catalysts against sintering. According to the literature [248], the formation of filamentous carbon is generally not associated with catalyst deactivation. This can be due to the Ni particles' dispersion at the tips of the filamentous carbon, which serves as a stabilizing mechanism, enabling the catalyst to maintain its activity for an extended period.

The bulk phase of the spent catalysts was identified using XRD (Figure 4.30a). The diffraction patterns revealed the presence of  $\text{SiO}_2$ ,  $\text{La}_2\text{O}_3$ , and metallic nickel components in the spent catalysts. However, all the spent catalysts exhibited a carbon (graphite) peak at  $2\theta$  of  $26.5^\circ$  [254]. These XRD patterns confirmed the formation of a carbon phase on the spent NSLF-x catalysts during the DRM process. The faint

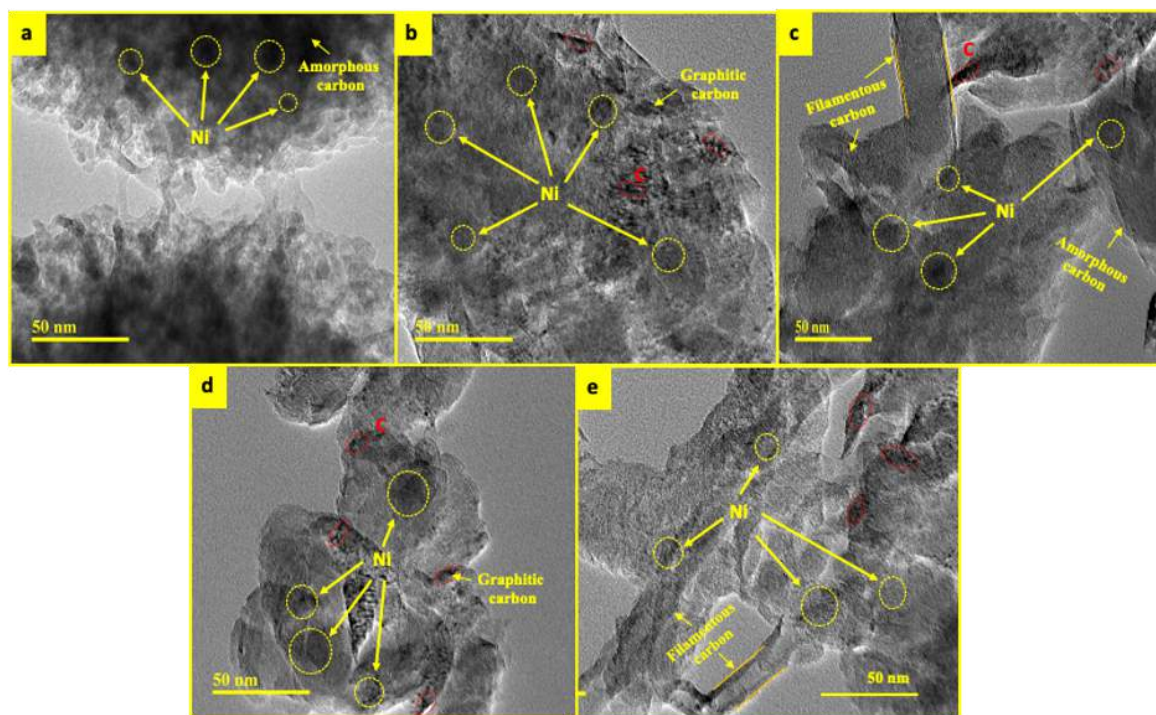


Figure 4.29: TEM images of the spent catalysts; (a) NSLF-3, (b) NSLF-6, (c) NSLF-8, (d) NSLF-11, (e) NSLF-15.

diffraction peak observed at  $26.5^\circ$  indicated a small amount of graphite carbon deposited on the catalytic surface. Notably, NSLF-11 demonstrated the most prominent graphitic peak compared to the other catalysts. The Raman spectra of the spent catalysts, as depicted in Figure 4.30b, provide evidence of the presence of carbon species, which indicates carbon deposition. The presence of graphite carbon is revealed by the graphite carbon band (G-band) at  $1585\text{ cm}^{-1}$ . Additionally, the disorder-generated band (D-band) at  $1348\text{ cm}^{-1}$  is associated with the deposition of  $\text{sp}^3$ -bonded carbon. The intensity of the bands in the spectra reflects the quantity of carbon present, while the  $I_G/I_D$  serves as an indicator of the degree of graphitization in carbon formations. Consequently, a higher  $I_G/I_D$  ratio suggests a greater tendency for the rapid formation of graphitic carbon compared to amorphous carbon. This higher rate of graphitic

carbon formation increases the catalytic sensitivity to deactivation [255]. The analysis of the Raman spectra ratios shows that graphitic and amorphous carbon coexist in all the catalysts. Notably, the NSLF-3, NSLF-8, and NSLF-15 catalysts showed the lowest  $I_G/I_D$  ratio and the smallest areas, with the smallest ratio observed for NSLF-3. This suggests that there is a minimal amount of carbon deposition on the NSLF-3, NSLF-8, and NSLF-15 catalysts, which is consistent with the TGA analyses. This type of carbon deposition exhibits a reduced possibility of deactivation. Figure 4.30c displays the TGA of the spent catalysts, conducted to examine the presence of coke deposits on the surfaces. The TGA patterns revealed the weight loss acquired during operation and the amount of carbon produced, which can be eliminated by oxidation to form  $\text{CO}_2$ . However, the process of weight loss can be divided into three regions at different temperatures, in which the loss in weight below 200 °C can be attributed to  $\text{H}_2\text{O}$  desorption, weight loss in the range of 200-500 °C can be attributed to the removal of oxidized amorphous carbon, and weight loss above 500 °C can be attributed to the gasification of graphitic coke. Previous studies have highlighted the significant influence of Ni size on the regulation of carbon deposits or extraction, in which smaller Ni crystalline phase catalysts tend to form fewer carbon formations [256]. Furthermore, the partial oxidation of the NSLF-3 and NSLF-6 catalyst results in the formation of metal oxides, leading to an increase in peak around 450 °C in the TGA analysis. NSLF-15 catalyst reveals a small amount of amorphous carbon accompanied by the presence of graphite carbon, as evidenced by a weight loss above 550 °C. The lower weight loss of NSLF-3, NSLF-8, and NSLF-15 suggests reduced carbon deposits, indicating improved catalyst stability and resistance to deactivation.

In addition, the DSC curves of the spent catalysts are shown in Figure 4.30 d. The curves illustrate the presence of exothermic peaks due to the oxidation of different carbonaceous species on the catalytic surface in the range of 450-700 °C. The slight shift observed in the peaks is due to the presence of varying quantities of carbonaceous species deposited on the surface, mainly amorphous and graphitic carbon in this temperature range [257], as supported by XRD and TGA, with NSLF-3 showing the lowest amount of the graphitic diffraction peak. Figure 4.31 depicts the N<sub>2</sub> adsorption-desorption isotherms and pore size distribution of the spent catalysts. The isotherms of the spent catalysts closely resemble those of the fresh catalysts, maintaining type IV isotherms with the presence of hysteresis loops. However, a noticeable decrease in pore volume and BET surface area was observed in the spent catalysts due to damage to the porous framework and pore plugging. NSLF-11 exhibited a relatively smaller impact on pore volume and BET surface area among the spent catalysts, although the pore size slightly shifted towards larger diameters compared to others. This can be attributed to the deposition of higher coke over its surface, as confirmed by TGA (Figure 4.30c). Furthermore, all spent catalysts showed an increase in pore diameter, likely resulting from pore destruction that produced larger pores. Additionally, the presence of destructive species led to pore geometry blockage and reduced pore volume. This larger pore size is crucial for achieving a higher mass transfer coefficient, enhancing catalytic performance [254]. This study suggests that the fibrous structure of the SLF support contributed to the catalyst's high activity and stability, primarily due to improved Ni dispersion, the presence of basic sites, and SMSI.

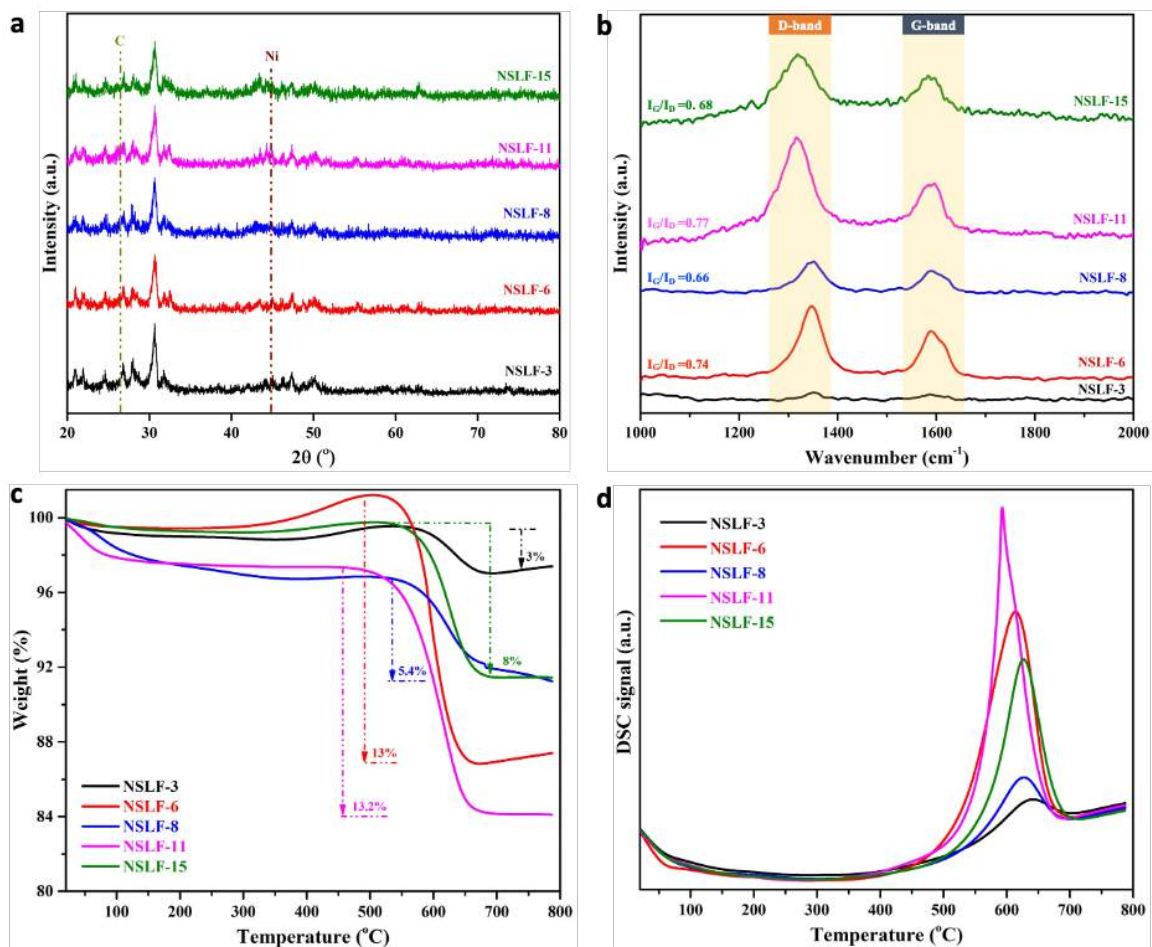


Figure 4.30: (a) XRD diffraction, (b) Raman spectra, (c) TGA profile, and (d) DSC curves of the spent NSLF-x catalysts.

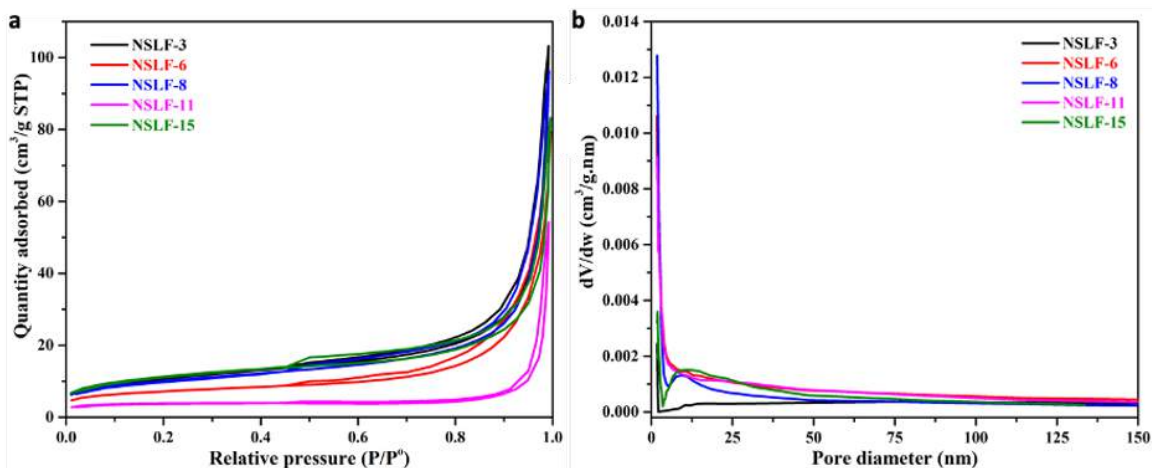


Figure 4.31: (a)  $\text{N}_2$  adsorption-desorption isotherms and (b) pore size distributions of the spent NSLF-x catalysts.

## CHAPTER 5

# CONCLUSIONS

In summary, we have developed the synthesis of a unique supported materials, achieved through a combination of  $\text{SiO}_2$  with pure  $\text{La}_2\text{O}_3$  and  $\text{ZnO}$ . This incorporation yields a distinctive core-fibrous shell morphology via microemulsion synthesis method. This strategy is responsible for enhancing textural properties, strengthening the interaction between Ni and developed supports, and increasing NiO dispersion. The core of the structure consists of  $\text{La}_2\text{O}_3$  or  $\text{ZnO}$ , while  $\text{SiO}_2$  forms the fibrous shell. Nickel species were subsequently introduced into the synthesized supports (SZF and SLF) using a wet impregnation approach to obtain Ni-based fibrous silica zinc oxide (NSZF) and Ni-based fibrous silica lanthanum oxide (NSLF) catalysts with varying Ni loading. The developed catalytic systems were tested for the DRM reaction. The influence of the amount of Ni loaded onto the SLF was evaluated to understand its influence on various factors such as structural durability, metal diffusion, active metal size, MSI, and accessibility of Ni NPs. Incorporating Ni and  $\text{ZnO}$  into the fibrous silica framework proved to be critical, significantly enriching the  $\text{O}_V$  on the catalyst surface. This alleviates Ni particle agglomeration and carbon deposition, as observed in the case of

the NSZF-10 and NSZF-15 catalysts. This incorporation also improves the textural properties and morphological structure of the 10 wt.% and 15 wt.% impregnated Ni over the SZF co-supported catalyst, resulting in SMSI, highly dispersed nickel over the SZF framework, and small Ni NP sizes. Therefore, these improved physicochemical properties play a critical role in boosting the NSZF-10 and NSZF-15 efficiency in DRM, exhibiting significantly high activity and stability. The conversion of CO<sub>2</sub> and CH<sub>4</sub> for the NSZF-10 catalyst reached 74% and 82%, respectively, while for NSZF-15, it reached 88.7% at the beginning of the reaction and 87% during the 40-h TOS at 750°C, with a high H<sub>2</sub>/CO ratio, without any sign of catalytic deactivation. Also, NSZF-10 and NSZF-15 catalysts exhibited minimal carbon deposition with negligible impact on its stability and without any morphological changes after the reaction period. Conversely, NSZF-3 showed a sign of deactivation after 37 h due to coke deposition influenced by its surface oxygen mobility, O<sub>V</sub>, and metal sintering, with the lowest surface area and Ni particle size influencing Ni sintering. Additionally, among the tested NSLF-x catalysts, the NSLF-15 catalyst exhibited exceptional performance, efficiency, and stability in the DRM process, achieving conversions of CO<sub>2</sub> (86.7%) and CH<sub>4</sub> (87%) without signs of deactivation even after 28 h of TOS. The addition of 15 wt.% Ni was identified as the optimal and most favorable Ni content for SLF. The characterization data provided evidence that the NSLF-15 catalyst exhibited a uniform dispersion of nickel species, resulting in a high number of active sites of metallic NiO. This favorable distribution of active sites facilitated the mass transfer of gaseous CH<sub>4</sub>/CO<sub>2</sub> within the catalyst. The uniform dispersion of the active phase has been proposed to be improved by the SMSI in the NSLF-15 catalyst, as demonstrated

by  $\text{H}_2$ -TPR. This interaction played a crucial role in maintaining the active NiO phase in a reduced state, leading to improved performance in the DRM. The enhanced NiO dispersion decreases the graphitic coke deposition and minimizes the production of non-filamentous coke, which affect catalyst performance. Taken together, the surface engineering optimization based on the core-fibrous shell structure of SZF and SLF show promise for high-performance DRM. Hence, this finding presents the NSZF-10, NSZF-15, and NSLF-15 catalyst for high-performance DRM and offers applicability for producing high-efficiency catalytic systems. With additional optimization of the material components and the amount of ZnO and  $\text{La}_2\text{O}_3$  incorporated, it is expected that the design of their structure will be further enhanced and applied in DRM.

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1. **MM Awad**, I Hussain , OA Taialla , SA Ganiyu , K Alhooshani , "Unveiling the Catalytic Performance of Unique Core-Fibrous Shell Silica-Lanthanum

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