

EFFECTS OF SiO_2 ENCAPSULATION ON $\text{Ni/MeO}_x\text{-Al}_2\text{O}_3$ FOR CO_2 (DRY) REFORMING OF METHANE

BY

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[This MS Thesis is dedicated to my beloved parents, Mr. and Mrs. Suleiman Alabi, my
dear siblings, and my fiancée, Lateefat.]

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LIST OF ABBREVIATIONS

DRM	Dry Reforming of Methane
TPR	Temperature Programmed Reduction
TPD	Temperature Programmed Desorption
NH ₃	Ammonia
XRD	X-ray Diffraction
BET	Brunauer–Emmett–Teller (Surface Area Analysis)
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetry
CNTs	Carbon Nanotubes
ML	Machine Learning
AI	Artificial Intelligence
MEOS	Methyl Orthosilicate
TEOS	Tetraethyl Orthosilicate
CFD	Computational Fluid Dynamics
SDG	Sustainable Development Goal
JCPDS	Joint Committee on Powder Diffraction Standards
CREC	Chemical Reactor Engineering Centre (riser simulator)
CH ₄	Methane
CO ₂	Carbon Dioxide
H ₂	Hydrogen
H ₂ O	Water

CO	Carbon Monoxide
Ni	Nickel
SiO ₂	Silicon Dioxide (Silica)
Ce	Cerium
Zr	Zirconium
Al ₂ O ₃	Alumina
CaO	Calcium Oxide
T	Temperature (K)
P	Pressure (atm or bar)
A.E	Activation Energy (kJ/mol)
k	Reaction Rate Constant
ΔH	Enthalpy Change (kJ/mol)
K _{eq}	Equilibrium Constant
R	Universal Gas Constant (8.314 J/mol·K)
E _{CH₄}	Activation Energy for CH ₄
E _{CO₂}	Activation Energy for CO ₂
E _{H₂}	Activation Energy for H ₂
E _{CO}	Activation Energy for CO
RWGS	Reverse Water–Gas Shift Reaction
SRM	Steam Reforming of Methane
POM	Partial Oxidation of Methane

ABSTRACT

Full Name : Sherif Alabi

Thesis Title : Effects of SiO₂ Encapsulation on Ni/MeO_x-Al₂O₃ for CO₂ (Dry)
Reforming of Methane

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Advancement in catalyst design for dry reforming of methane (DRM) has positioned the process as an innovative and sustainable pathway for converting two major greenhouse gases, CH₄ and CO₂, into syngas. This enables the conversion of syngas into valuable chemicals and fuels. DRM offers an alternative approach for hydrogen production which aligned with global emission reduction goal, particularly SDG 13: climate action. However numerous challenges have been faced on the deactivation, stability and coke resistance of the catalyst. To address these challenges, recent advancements have focused on developing robust catalyst structures, through silica encapsulation. This approach involves the encapsulation of Ni-based catalysts in a mesoporous silica shell which creates a barrier that inhibits Ni sintering and reduces coke formation. In this study, the effect of silica encapsulation was investigated on Ni/Ce-Al₂O₃, Ni/CaO-Al₂O₃ and Ni/Ce-Zr catalysts. The catalyst was evaluated at 650 °C using the CREC riser simulator, focusing on CH₄ and CO₂ conversion, H₂ and CO yield. Among the tested catalysts, the silica-encapsulated pairs demonstrated significantly higher conversion and minimal coke deposition, as confirmed by TGA and TEM analysis. Notably, all catalyst pair shows high stability over 10 consecutive repeated cycles of continuous reaction without regeneration, maintaining over 95 % of their initial activity. These findings highlight the potential of SiO₂ encapsulated catalyst in improving DRM catalyst performance.

ملخص الرسالة

الاسم الكامل: شريف الابي

عنوان الرسالة: في عملية الإصلاح الجاف لثاني أكسيد $\text{Ni/MeO}_x\text{-Al}_2\text{O}_3$ على محفز SiO_2 تأثير تغليف الكربون والميثان

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: رجب ١٤٤٦ هـ

في ترسيخ هذه التقنية كمسار مبتكر (DRM) لقد ساهم التقدم في تصميم المحفزات لعملية الإصلاح الجاف للميثان إلى، CO_2 وثنائي أكسيد الكربون (CH_4) ومستدام لتحويل اثنين من أبرز غازات الاحتباس الحراري، وهما الميثان ويُستخدم هذا الغاز في إنتاج مواد كيميائية ووقود ذات قيمة عالية. وتُعد عملية الإصلاح (syngas) غاز التخليق الجاف للميثان بديلاً واعدًا لإنتاج الهيدروجين، بما يتماشى مع أهداف تقليل الانبعاثات العالمية، لا سيما الهدف الثالث عشر من أهداف التنمية المستدامة (العمل المناخي). (ومع ذلك، تواجه هذه التقنية تحديات كبيرة تتعلق بتعطيل نشاط المحفزات، واستقرارها، ومقاومتها لتكوين الكربون. ولمعالجة هذه التحديات، ركزت الأبحاث الحديثة على تطوير هياكل محفزات أكثر صلابة من خلال تقنية التغليف بالسيليكا. وتتمثل هذه التقنية في تغليف محفزات النيكل بقشرة من السيليكا المسامية، تعمل كحاجز يمنع تلبد جزيئات النيكل ويحد من تكوين الكربون. في هذه الدراسة، تم التحقيق في تأثير التغليف تم تقييم أداء هذه Ni/Ce-Zr و $\text{Ni/CaO-Al}_2\text{O}_3$ و $\text{Ni/Ce-Al}_2\text{O}_3$: بالسيليكا على ثلاثة أنواع من المحفزات مع التركيز على معدلات تحويل، CREC riser simulator باستخدام جهاز $^\circ\text{C}$ المحفزات عند درجة حرارة 650 أظهرت النتائج أن المحفزات المغلفة بالسيليكا سجلت معدلات تحويل CO و H_2 بالإضافة إلى إنتاج CO_2 و CH_4 ومن الجدير بالذكر أن TGA و TEM أعلى بكثير، مع ترسيب كربوني طفيف، كما تم تأكيد ذلك من خلال تحاليل جميع المحفزات المغلفة أظهرت استقرارًا عاليًا خلال عشر دورات تفاعل متتالية بدون إعادة تنشيط، محافظةً على في SiO_2) أكثر من 95% من نشاطها الأصلي. وتؤكد هذه النتائج الإمكانات الواعدة لمحفزات النيكل المغلفة بالسيليكا تحسين أداء المحفزات في تفاعلات الإصلاح الجاف للميثان.

CHAPTER 1

INTRODUCTION

The global energy demand is projected to increase significantly in the coming decades, driven by rapid urbanization, industrialization and population growth. This subsequently leads to high demand for energy and fossil-fuel based energy has been the driven world source of energy. To meet up with the current SDG-17 goals on low emission of greenhouse gas a sustainable energy system needs to be adopted [1], [2]. Different innovative conversion technologies for the conversion of light hydrocarbon specifically methane to produce hydrogen for energy production have been studied by various research groups. Among these methods includes SRM, POM, and DRM. In SRM, water is used as an oxidant to generate hydrogen and is most widely used in industries. Despite SRM technology offers high product yield, it requires significant energy input and is highly endothermic, resulting to a syngas product of H_2 to CO ratio of 3, which is too high for optimal the Fischer-Tropsch reaction. POM on the other hand, is a method that utilizes the oxidation of methane at lower temperature as compared to SRM. Conversely, DRM utilizes CO_2 for conversion of methane to produce syngas, capturing two major greenhouse gases (CH_4 and CO_2) in the process. This syngas can be further converted to value added chemical like methanol, light olefins, and aromatics via Fischer–Tropsch reactions as the H_2/CO ratio is low and compatible with the reaction as compared to that obtained from SRM [3].

Precious metal catalysts, including Pt, Ru, and Rh, typically demonstrate high activity and exhibit significant resistance to carbon deposition on DRM reaction. Nonetheless, their high cost limits their usage as they are not economically viable for industrial production. On the other hand, nonprecious metal catalysts like Ni and Co offer moderate activity for DRM but are at risk of deactivation from carbon deposition and catalyst sintering. To address these issues and enhance practical DRM applications, various strategies have been proposed, such as addition of promoters, bimetallic catalysts, optimizing strong catalyst-support interactions and encapsulation of the catalyst with mesoporous silica [4].

As part of the recent strategic practice in developing a high performing catalyst with little or no coke formation and high stability, encapsulating the catalyst in an inorganic shell has proven effective to prevent coke formation by acting as a proactive barrier. Hence, strong resistance to coke in DRM is provided by a core@shell structure, which is produced by covering the catalyst with porous materials such as SiO_2 and Al_2O_3 . This structure minimizes heat agglomeration of the core Ni catalyst by confinement. Excellent catalytic activity and coke resistance were established by Kosari et al. for nickel silicate hollow spheres with thin shells and extensive internal cavities [5], [6]. Additionally, Liu et al., developed a novel core-shell catalyst by utilizing Ni-ZrO₂ as the core and microporous silica as the shell. This catalyst demonstrated zero coke formation and effectively prevented sintering of the Ni nanoparticles. Hence, the Ni-ZrO₂@SiO₂ catalyst exhibits high potential for industrial applications because of its remarkable anti-sintering capabilities and resistance to carbon deposition [7].

In this work, we prepared three catalyst sets, Ni/Ce-Al₂O₃, Ni/CaO-Al₂O₃, and Ni/Ce-Zr with a Nickel loading of 5% and further encapsulating each catalyst on a SiO₂ shell. The catalyst was further screened using the CREC riser simulator and they all show high catalyst activity

and performance with Ni/CaO-Al₂O₃ outperforming others. The loading of the best performing catalyst was then increases and further thermodynamics and kinetic studies was carried out on both Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂

1.1 Thesis problem statement

Carbon dioxide (CO₂) is a significant greenhouse gas, emitted in large volumes during activities such as oil and gas production, power generation, transportation, and industrial processes like cement manufacturing. As the world's largest oil producer, Saudi Arabia faces the dual challenge of CO₂ capture and utilization to maintain environmental safety and align with global standards. CO₂ reforming is a promising approach to mitigate this emission. Methane on the other hand can also be capture via the master gas capture system (MGS) in support of the country's commitment to reducing emissions under the vision 2030 and attaining zero routine flaring commitment. By also aiming to utilize more of its gas reserves, Dry reforming of methane can serve as an alternative of diversify the use of natural gas and CO₂ capture from various oil production sectors for synthetic gas production which can then be further processed to produce valuable fuels and chemicals.

DRM encounters several challenges, including the requirement for high operating temperatures, coke formation leading to catalyst deactivation, metal-support interactions, and catalyst stability issues. This research proposal seeks to address these challenges by developing a nickel-based catalyst encapsulated within a silica shell. The proposed catalyst is designed to exhibit exceptional coke resistance and superior performance, ensuring high activity, selectivity, and hydrogen yield under DRM conditions.

1.2 Thesis objectives

The primary aim of this work is to develop a Novel Ni-based catalyst and further encapsulate the catalyst within a mesoporous silica shell to improve the catalyst performance of the conventional catalyst for DRM. The catalyst performance and properties were studied on the following specific objectives:

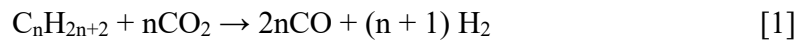
- To synthesize Ni-based catalysts supported on Ce-Al₂O₃, CaO-Al₂O₃, and Ce-Zr for DRM
- To synthesize core-shell structured catalysts by encapsulating Ni-based catalyst with SiO₂ using the Stöber method.
- To characterize the catalysts using techniques such as H₂-TPR, NH₃-TPD, BET surface area analysis, XRD, TGA, SEM, and TEM.
- To assess the catalytic performance of both encapsulated and non-encapsulated catalysts in a CREC riser simulator
- To evaluate stability over repeated cycles and characterize the spent catalysts. |

CHAPTER 2

LITERATURE REVIEW

2.1 Dry reforming of light hydrocarbons

Dry reforming of specifically light hydrocarbons (methane, ethane and propane) represents a significant advancement in the mitigation of greenhouse gases (GHG) which is deteriorating the ozone layer in the environment. This innovative process uses CO₂ to produce syngas. Eq. 1 represents the general equation of dry reforming reaction.



Eq. 2 represents the dry reforming of methane (DRM). Methane reacts with CO₂ to produce syngas.



During DRM, the ratio of the syngas components (CO and H₂) is expected to be 1 from the stoichiometry, but the ratio is always less than 1 due to the reverse water-gas shift (RWGS) reaction.



Carbon is produced during dry reforming (Eq. 4), and it can be classified to be in a filamentous form. The presence of this form of carbon leads to results in the deactivation of the catalyst and reactor blockage. The carbon produced is solely from the decomposition of CH₄ and Boudouard reaction which is the disproportionation of CO to form carbon and CO₂ (Eq. 5).



Other light hydrocarbon dry reforming has been carried out to synthesis syngas using various types of catalyst. DR of ethane, propane and butane is represented in Eq. 6, 7 and 8 respectively



Similarly, to Eq. 4 and 5, carbon is also deposited on the catalyst during the dry reforming of other light hydrocarbons as shown by Eq. 9, 10 and 11.



2.2 Reactor type for dry reforming

2.2.1 Fixed bed reactor

Fixed-bed reactors are a type of reactors which are commonly used in the chemical industry for heterogeneous catalysis. The packing in the reactor can be in different shapes ranging from cylinders, spheres, Raschig-rings or complex shapes. The arrangements can be structured or random in the column. The particle size and tube diameter influence the behavior of the fluid in the reactor [8]. In highly endothermic and exothermic reactions, the ratio of tube-to-particle diameter is typically low and the temperature, species distribution, flow and rate of reaction are affected by the effect of the tube-to particle size. High pressure drops and volume flow constrains the particle diameter. For reactors that involve higher temperatures either

exothermic or endothermic, heat transfer either from or to the reactor must be considered. Eppinger et al. [8] conducted numerical investigations of operating conditions in a fixed-bed reactor for DRM, revealing minimal catalyst deactivation from coke formation. This setup enabled high selectivity for hydrogen and effective conversion of CH_4 and CO_2 . In related findings, Zhou et al. introduced a novel Ru/CeO_2 catalyst synthesized via microwave-assisted hydrothermal methods for DRM in a fixed-bed reactor, achieving high activity with CH_4 and CO_2 conversions of 58% and 71%, respectively, and an H_2/CO ratio exceeding 0.85 at 600°C over 120 hours. This approach demonstrates potential for DRM commercialization and coke resistance at relatively low temperatures [9]. A typical setup of a fixed bed reactor for DRM is shown in Figure 2.1.

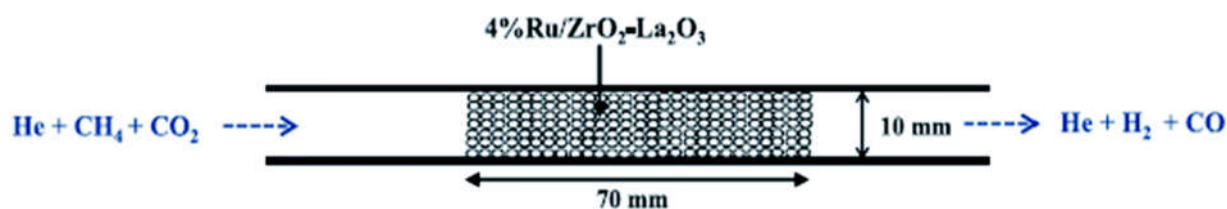


Figure 2.1: Typical fixed bed reactor (Adapted from [10]).

2.2.2 Fluidized bed reactor

Fluidized-bed reactors have been proved both theoretically and experimentally as an excellent choice of reactors for extreme condition reactions, these reactions include highly exothermic reactions. Compared to fixed-bed reactors, fluidized-bed reactors offer significant performance because of turbulent flow of gas and high circulation rate in the reactor. In recent times, fluidized bed reactors have been majorly used by researchers in the DRM using different catalysts and supports system. Pacifico et al., carried out $\text{CH}_4\text{-CO}_2$ reforming using a formulated nickel catalyst system (Ni-NiO (4.82% wt.)/ $\gamma\text{-Al}_2\text{O}_3$) in a fluidized bed reactor at

700 °C and 1 atm. The reactor operation was evaluated experimentally using the fluidization regime. The minimum and maximum fluidization was evaluated at 700 °C as 0.31×10^{-2} and $1.8 \times 10^{-2} \text{ ms}^{-1}$ respectively. High CH_4 and CO_2 conversion was achieved in the reactor with high H_2 and CO yield of 47.72 and 49.95 % respectively. This leads to the formation of 97.67 % yield of syngas [11].

Furthermore, the two-zone fluidized bed reactor (TZFBR) has been applied extensively for CO_2 reforming, providing a different configuration reaction configuration as compared to CFBR. The TZFBR has two zones with distinct atmosphere created by means of two feeds inlet as illustrated in Figure 2b. This reactor design effectively addresses the coke deactivation on the catalyst surface by facilitating coke formation in the upper zone while regenerating deposited coke in the lower zone through the introduction of an oxidizing gas such as O_2 , CO_2 , or H_2O [12]. Operating under optimized and suitable conditions enables simultaneous catalyst regeneration and the main reaction occurring, hence, showcasing process intensification.

An improvement to the TZFBR involves the addition of membranes for selective product removal. Hydrogen selective membranes have been studied by several researchers in a fluidized bed reactor. A well-established membrane reactor has been incorporated into TZFBR configuration (TZFBR + MB) as illustrated in Figure 2c [13].

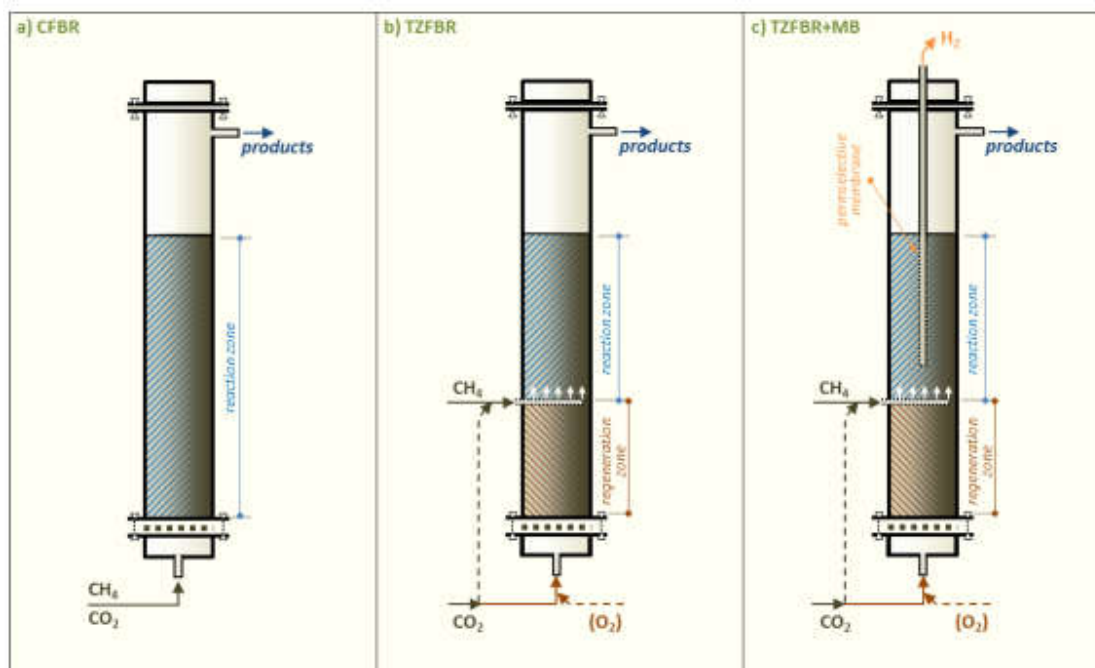


Figure 2.2: Fluidized bed reactor configuration: a) Conventional Fluidized Bed Reactor (CFBR), b) Two-Zone Fluidized Bed Reactor (TZFBR), c) Two-Zone Fluidized Bed Reactor with membranes (TZFBR + MB) [13].

2.2.3 CREC-Riser simulator

The Chemical Reaction Engineering Centre CREC riser simulator is a novel fluidized lab scale reactor which was developed in 1992 at the University of Western Ontario. This reactor is aimed at evaluating catalyst performance under a typical short time of 2-20 s. The reactor has been fully applied in different catalytic reaction studies including the dry reforming, steam reforming, chemical looping combustion, catalytic desulphurization of gasoline, biomass gasification and so on. In the riser simulator, the impeller which was placed at the upper section and on rotating, it tends to create upward and downward gas flows at the center and periphery respectively. The particles in the basket located at the center of the reactor are fluidized under

the normal upward gas flow conditions. Under high impeller speed (5500 -6000 rpm), a nearly constant concentration of reactants is attained for all gas phase species. The design of the reactor allows both the fluidized particles and high gas mixing [14].

The schematic of the riser simulator is presented in Figure 2.3, illustrating the injection point (capable of injecting gas and liquid samples), the vacuum box (used for temporary storage of the product before sending to the gas sampling loop), four point valve 4PV (an automated valve connecting the reactor and vacuum box, this valve opens at end of the reaction time) and six point valve 6PV (used to direct the gas to the gas chromatography for analysis). The general assembly of the CREC Riser Simulator provides an efficient injection approach, controlled catalytic reaction conditions, instant product transport and an on-line analysis of the product using gas chromatography [15].

Figure 2.4 represents the geometry of the reactor bucket displaying the internal components of the basket. Assumptions have been made by literature suggesting that the thickness of the basket vertical baffles and impeller blades are negligible.

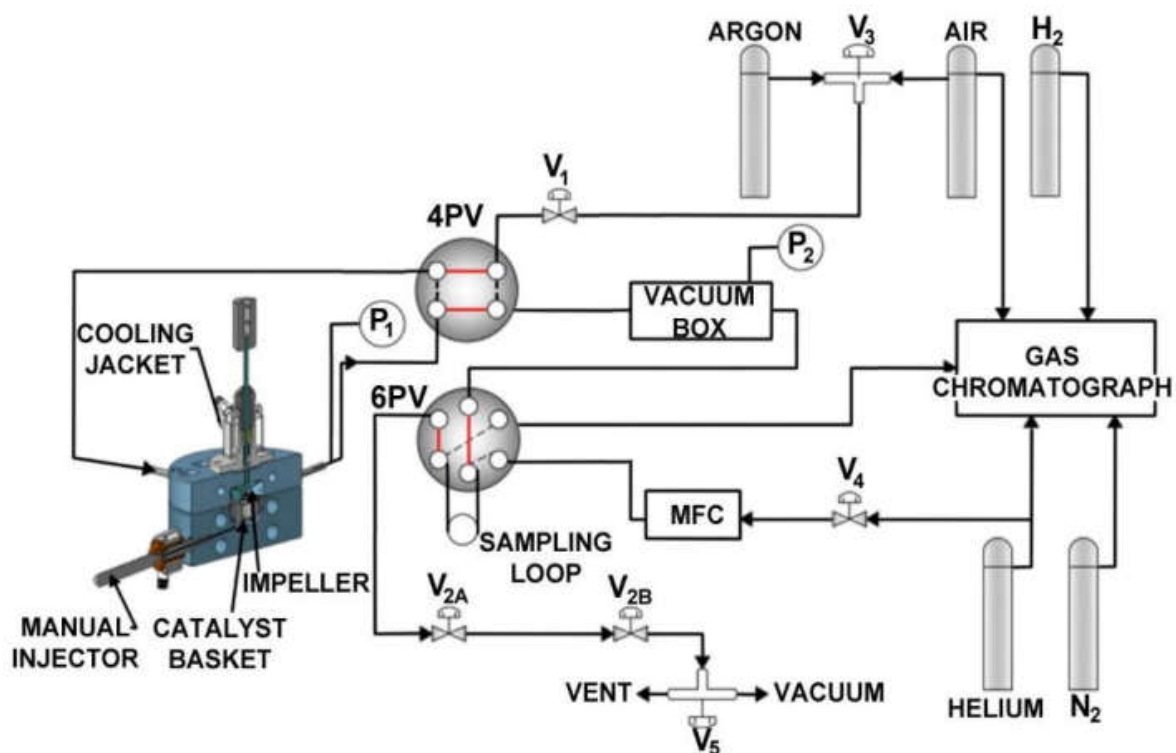


Figure 2.3: Schematic representation of the CREC riser reactor system [14].

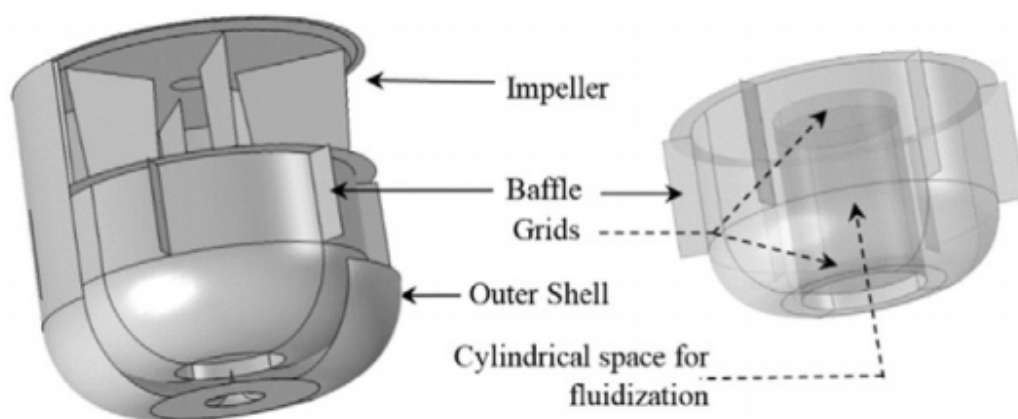


Figure 2.4: Geometry of the reactor basket used in the CREC Riser [15]

2.3 Thermodynamics

Thermodynamics study is essential in CO₂ reforming for evaluating the optimum parameters needed for having higher product yield. For DRM reaction, high temperatures are required for carbon dioxide and methane conversion into syngas. Moreover, most reported studies indicate that the optimal performance of Ni-based catalysts occurs at temperatures ≥ 800 °C. Thus, the use of catalysts can decrease the required energy to achieve high yield of syngas. Table 2.1 presents the possible reactions in DRM. Chemical equilibrium and thermodynamic analysis indicate that these reactions are highly endothermic and involves an increase in gas volume. Therefore, high temperature and low-pressure conditions are required for driving the reaction toward syngas production [16], [17]. In this regards, CO₂ and CH₄ molecules possess significant dissociation energy and high stability, thus high temperature is needed to attain equilibrium conversion to syngas. Additionally, the equilibrium is influenced by side reactions such as the reverse water–gas shift (RWGS) reaction, which often enhances CO₂ conversion more than CH₄, resulting in an H₂/CO ratio of 1 or lower [18].

However, carbon formation is a significant contributor to catalyst deactivation of DRM. The two main pathways for carbon formation include methane decomposition and the Boudouard reaction (CO disproportionation). Low oxygen availability further promotes surface carbon buildup. While carbon formation is more likely below 800 °C, higher temperatures shift the mechanism toward CH₄ decomposition as the dominant carbon source. Therefore, controlling temperature, pressure, and feed composition (CH₄/CO₂ ratio) is essential for minimizing carbon accumulation and optimizing DRM efficiency [16].

The thermodynamic equilibrium study reported by Adamu et al., reveals key insight on the effect of temperature on DRM at feed composition of 1:1 ($\text{CH}_4:\text{CO}_2$). At lower reforming temperatures (500 °C), conversion of CO_2 is minimal, the equilibrium composition of CO_2 is peak at 600 °C which suggest operating at this temperature is optimum for maximum hydrogen yield. High coke formation is observed at lower temperature and almost zero at temperature of 1250 °C. At this condition, 99 % of hydrogen from CH_4 is recovered as gaseous hydrogen and the syn gas ratio remains constant from 900 °C to 1500 °C as shown in Figure 2.5. This highlights the temperature optimization of catalyst development for efficient CO_2 reforming [19].

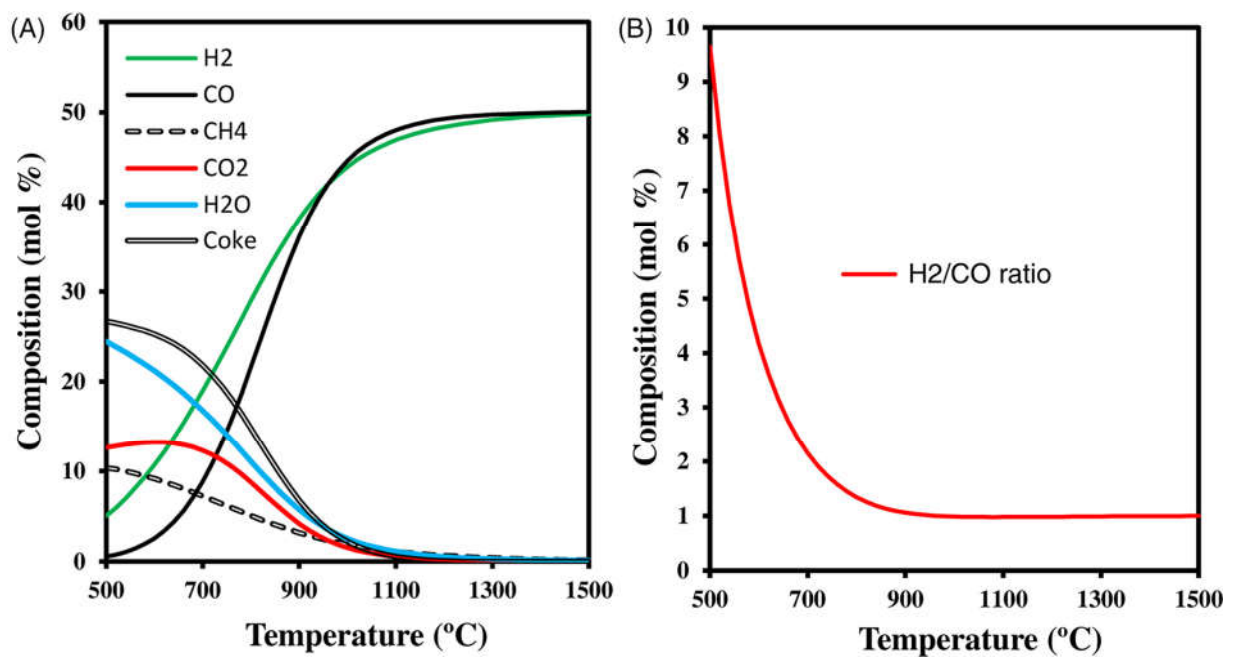


Figure 2.5: Thermodynamic results for dry reforming of methane ($\text{CH}_4:\text{CO}_2 = 1:1$). (A) Equilibrium product composition; (B) Syngas (H_2/CO) ratio as a function of temperature [19].

Table 2.1: Different possible reactions during DRM [20]

S/ No	Reactions	ΔH_{298K} kJ/mol	Ln (K _{eq}) at 573K	Ln (K _{eq}) at 1373	Favored by
1.	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247	-20	13	High Temperature
2.	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	41	-5	2	High Temperature
3.	$2\text{CH}_4 + 2\text{CO}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O}$	284	-36	0	High Temperature
4.	$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	136	-14	4	High Temperature
5.	$2\text{CH}_4 + \text{CO}_2 \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO} + \text{H}_2\text{O}$	106	-19	-5	High Temperature
6.	$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-49.1	-12	-20	Low Temperature
7.	$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	-90.6	-10	-20	Low Temperature
8.	$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	-172.4	15	-7	Low Temperature
9.	$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	74.9	-6	5	High Temperature
10.	$\text{H}_2 + \text{CO} \rightleftharpoons \text{H}_2\text{O} + \text{C}$	-131.3	12	-6	Low Temperature
11.	$\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$	-90	8	-5	Low Temperature
12.	$3\text{H}_2\text{O} + \text{CH}_3\text{OCH}_3 \rightleftharpoons 2\text{CO}_2 + 6\text{H}_2$	136	20	37	High Temperature
13.	$\text{CH}_3\text{OCH}_3 + \text{CO}_2 \rightleftharpoons 3\text{CO} + 3\text{H}_2$	258.4	10	40	High Temperature
14.	$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	-37	3	-1	Low Temperature
15.	$\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2$	204.8	14	37	High Temperature
16.	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	-206.2	14	-11	Low Temperature
17.	$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	-165	14	-10	Low Temperature

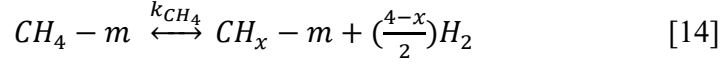
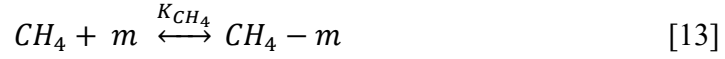
2.4 DRM Reaction mechanism and kinetics

The study of the kinetics and reactions involved in DRM is essential to both the academic and industries, as it helps in understanding the reaction mechanisms. The derived mechanism for DRM should be capable of predicting rate of product formation, assessing reactant conversion and providing details on how reactants are adsorbed and desorbed on the catalyst surface [21], [22]. shows a schematic representation of some DRM reaction pathways. Various reaction models are available across the literature to represent this reaction. These models include, the power law (PL), Langmuir Hinshelwood (LH), and Eley Rideal (ER I and ER II). Among these, the power law model is the most straightforward approach for describing the rate of the DRM reaction. Although it lacks mechanistic depth, it is often employed to estimate the apparent reaction rate constant. The mathematical expression for the PL model is provided in Eq. 12.

$$R=k[P_{CH_4}]^m[P_{CO_2}]^n \quad [12]$$

Where m and n represent the reaction orders that vary with respect to the type of catalyst used. R denote the overall reaction rate, P_{CH_4} and P_{CO_2} correspond to the partial pressures of methane and carbon dioxide.

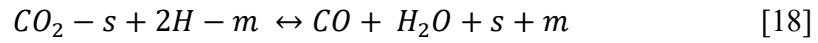
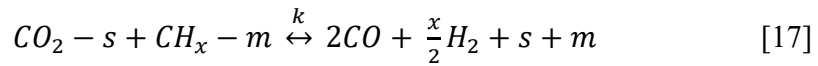
The LH model is generally used to represent the kinetic of DRM. This model suggest that the catalyst active sites facilitate absorption of the reactants and subsequent dissociation of the reactant. In this model, the decomposition of CH_4 and CO_2 is an elementary reaction step, with multiple surface intermediates assumed to be in thermodynamic equilibrium. Based on the bifunctional mechanism proposed by Wang et al. for a Ni-CaO-ZrO₂ catalyst, the dry reforming of methane proceeds according to the following kinetic expressions.



CO₂ adsorption



Surface reaction of the activated CH₄ and CO₂, while RWGS reaction occurs

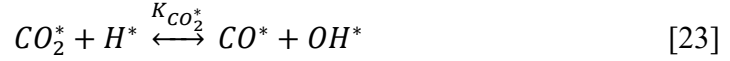


Wang et al., expressed Langmuir–Hinshelwood kinetic rate equation base on the above mechanism as:

$$r_{CH_4} = \frac{kK_{CH_4}k_{CH_4}K_{CO_2}P_{CH_4}P_{CO_2}}{K_{CH_4}k_{CH_4}K_{CO_2}P_{CH_4}P_{CO_2} + K_{CH_4}k_{CH_4}P_{CH_4} + kK_{CO_2}P_{CO_2}} \quad [19]$$

In contrast, Wei et al. proposed a reaction mechanism based on a Ni–MgO catalyst, outlining the following kinetic pathway for DRM





In these mechanisms, experimental evidence indicates that CH₄ dissociation (Eq. 21) is the rate-determining step (RDS). Based on the pseudo-steady-state hypothesis (PSSH), the net formation rate of surface intermediates is assumed to be negligible. Consequently, the overall reaction rate for DRM is expressed in terms of CH₄ consumption, as shown in Eq. 27 [23]

$$r_{CH_4} = K_{CH_4} k_2 [CH_4] \left(\frac{C_{MT}}{M} \right)^5 \quad [27]$$

$$\text{where } M = 1 + K_{CH_4} [CH_4] + K_{CO_2} [CO_2] + \frac{[CO]}{K_{CO}} + \left(\frac{[H_2]}{K_{H_2}} \right)^{0.5} + \frac{[CO]^2}{a K_{CO} [CO_2]} + \frac{a [CO_2] [H_2]^{0.5}}{[CO] K_{H_2}^{0.5}}$$

$$a = K_{CO_2} K_{CO_2^*} K_{C^*} K_{CO}.$$

C_{MT} = total concentration of catalyst active sites

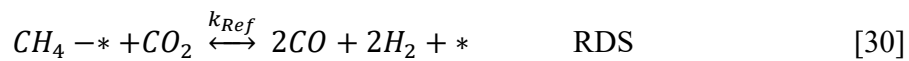
In ER model, one reactant is assumed to be adsorbed on the catalyst surface at adsorption equilibrium. The rate-determining step (RDS) involves the reaction between the adsorbed species and the other reactant from the gas phase resulting in formation of products. Theoretically, since only one reactant can be adsorbed, two variations of the models are considered (ER I and II). ER I, gaseous CO₂ reacting with adsorbed CH₄, and ER II, where

gaseous CH_4 reacting with adsorbed CO_2 . The ER I and II mechanism and rate laws are shown below as reported by

Furthermore, the Eley–Rideal (ER) model assumes that only one of the reactants is adsorbed on the catalyst surface at adsorption equilibrium, while the other remains in the gas phase. The rate-determining step (RDS) involves the interaction between the adsorbed species and the gaseous reactant to form the product. Since the model allows for the adsorption of only one reactant, two variations are commonly considered: ER I, where gaseous CO_2 reacts with adsorbed CH_4 , and ER II, where gaseous CH_4 interacts with adsorbed CO_2 . The reaction mechanisms and corresponding rate expressions for both ER I and ER II are presented below, as proposed by [24].



Eley–Rideal model I (ER I):

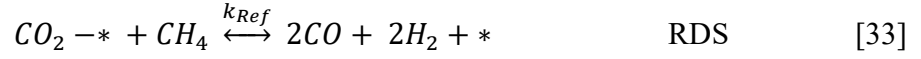


Therefore, the ER I rate of reaction is given

$$r_{Ref} = \frac{k_{Ref} K_{CH_4} (P_{CH_4} P_{CO_2} - \frac{P_{CO}^2 P_{H_2}^2}{K_{Ref}})}{1 + K_{CH_4} P_{CH_4}} \quad [31]$$

Eley–Rideal model II (ER II):





$$r_{Ref} = \frac{k_{Ref} K_{CO_2} (P_{CH_4} P_{CO_2} - \frac{P_{CO}^2 P_{H_2}^2}{K_{Ref}})}{1 + K_{CO_2} P_{CO_2}} \quad [34]$$

The analysis above clearly demonstrates that DRM encompasses several mechanistic routes, and the choice of catalyst strongly influences the applicable kinetic model. Kinetic studies are crucial for comprehending catalytic activity even though they show distinct pathways for various catalysts. This information eventually advances the industrialization of DRM catalysts by enabling the more efficient and stable catalysts to be designed. Table 2.2 shows the kinetic parameters of Nickel based catalyst from recent findings.

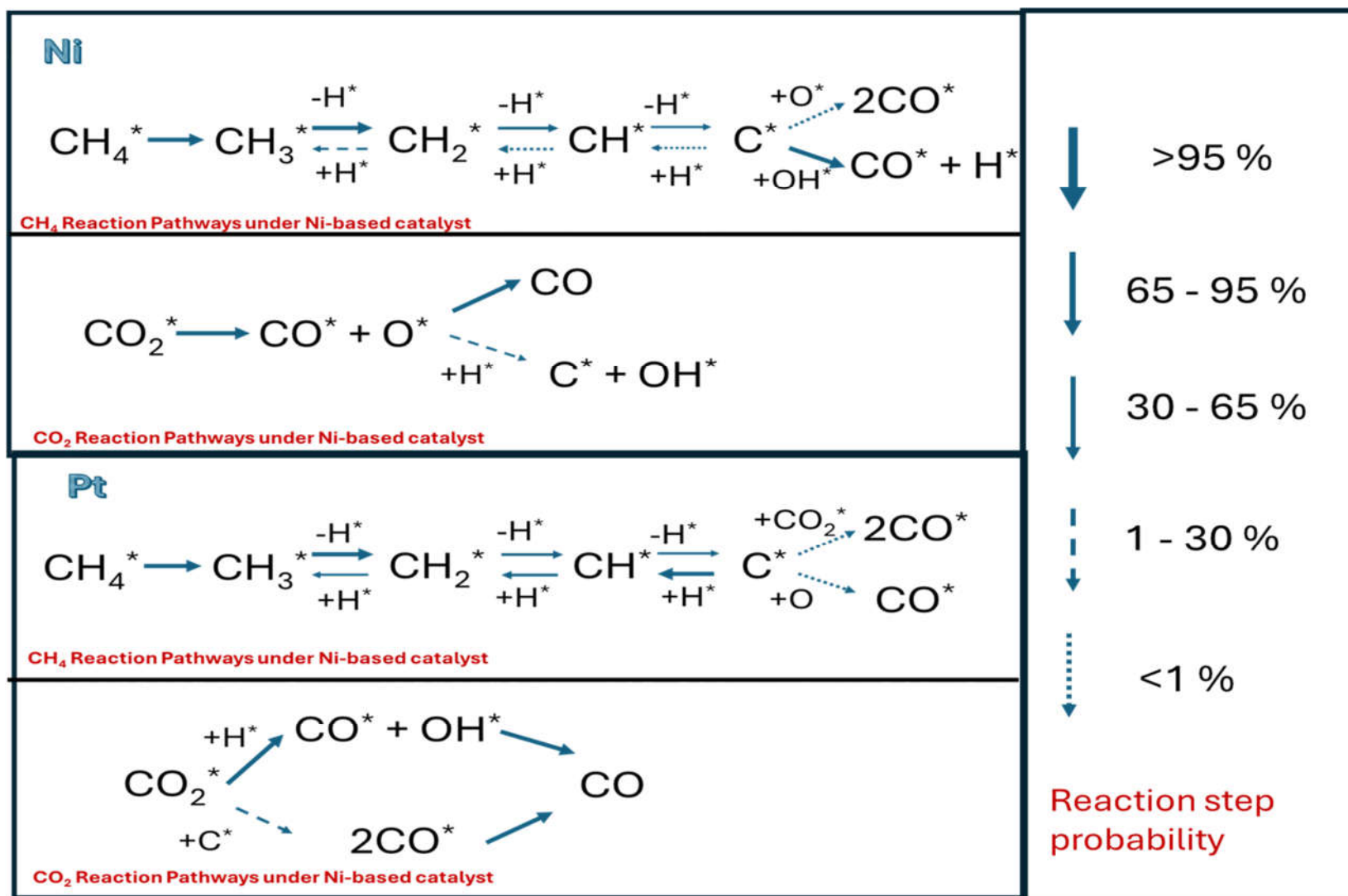


Figure 2.6: Comparative reaction pathways of CO₂ and CH₄ illustrating the distinct DRM mechanisms observed on different active metal surfaces. Adapted from [25].

Table 2.2: Kinetics parameter of Nickel based catalyst from literature

S/N	Catalyst	Method of preparation	Model name	Temp	k	AE (kJ/mol)	Ref.
1.	Li ₆ Zn _{0.7} Ni _{0.3} O ₄		Avrami-Erofeev model	550-750	$1.35 \times 10^{-2} \text{ s}^{-1}$		[26]
2.	Ni-ZrO ₂ /MCM-41		Power law	500-800	$k_1 = 7.3 \text{ l}^{-1} \text{ gmcat}^{-1} \text{ h}^{-1}$ $k_{-1} = 3.6 \text{ (mol. l}^{-1} \text{ h}^{-1})$	E _{CH4} = 47.4	[27]
3.	Ni/Al ₂ O ₃		Power law	750-850		E _{CH4} = 69.1 ± 20.2	[28]
4.	Ni/MgO/CeZrO		Power law	750-850		E _{CH4} = 67.4 ± 3.4	[28]
5.	NiMg/Al	Impregnation	Langmuir Hinshelwood Hougen Watson	600-800	$1.38 \times 10^2 e^{\frac{-28000}{RT}}$ (mmol g ⁻¹ h ⁻¹ hPa ⁻²)	E _{CH4} = 117.15	[29]
6.	Ni/Ce	Impregnation	Langmuir Hinshelwood Hougen Watson	600-800	$3.82 \times 10^2 e^{\frac{-2550}{RT}}$ (mmol g ⁻¹ h ⁻¹ hPa ⁻²)	E _{CH4} = 10.67	[29]
7.	Ni/SBA	Impregnation	Langmuir Hinshelwood Hougen Watson	600-800	$5.79 \times 10^8 e^{\frac{-1180}{RT}}$ (mmol g ⁻¹ h ⁻¹ hPa ⁻²)	E _{CH4} = 4.94	[29]
8.	Ni _{0.7} Mg _{0.93} O-R	Solvothermal synthesis	Power law	600-800		E _{CH4} = 87	[30]
9.	Fe _{0.009} Ni _{0.061} Mg _{0.93} O-R	Solvothermal synthesis	Power law	600-800		E _{CH4} = 101	[30]
10.	Fe _{0.012} Ni _{0.058} Mg _{0.93} O-R	Solvothermal synthesis	Power law	600-800		E _{CH4} = 123	[30]

11.	Ni/MgO-A	Incipient wetness impregnation	Power law	873	$0.2 \text{ s}^{-1} \text{ kPa}^{-1}$	$E_{\text{CH}_4} = 105$	[31]
12.	Ni-SiO ₂	Incipient impregnation	pseudo-first-order reaction rate for CH ₄	400 - 900		$E_{\text{CH}_4} = 80.28$	[32]
13.	Ni ₅ /SBA-15	Wet impregnation	Power law	580 - 620	$2.73 \text{ mmol.g}^{-1}.\text{s}^{-1}.\text{atm}^{-(a+b)}$	$E_{\text{CH}_4} = 35.11$	[33]
14.	Ir _{0.1} -Ni ₅ /SBA-15	Wet impregnation	Power law	580 - 620	$10.53 \text{ mmol.g}^{-1}.\text{s}^{-1}.\text{atm}^{-(a+b)}$	$E_{\text{CH}_4} = 26.33$	[33]
15.	Ni-0.16B/Al ₂ O ₃	Impregnation	Langmuir–Hinshelwood–Hougen–Watson (LHHW) model	700-750		$E_{\text{CH}_4} = 52.54$	[34]
16.	Ni/Al	Wet impregnation	Power law	650 – 800	$k_{\text{H}_2} = 9.23 \pm 2.75$ ($\mu\text{mol}/(\text{s.gNi}))(k\text{Pa})\text{-a}$ $k_{\text{CO}} = 3.68 \pm 1.23$ ($\mu\text{mol}/(\text{s.gNi}))(k\text{Pa})\text{-(b+c)}$	$E_{\text{H}_2} = 36.23 \pm 3.28$ $E_{\text{CO}} = 50.76 \pm 3.12$	[35]
17.	1.1_2DMo-Ni/Al	Wet impregnation	Power law	650 - 800	$k_{\text{H}_2} = 18.00 \pm 6.38$ ($\mu\text{mol}/(\text{s.gNi}))(k\text{Pa})\text{-a}$ $k_{\text{CO}} = 4.87 \pm 2.29$ ($\mu\text{mol}/(\text{s.gNi}))(k\text{Pa})\text{-(b+c)}$	$E_{\text{H}_2} = 64.69 \pm 4.23$ $E_{\text{CO}} = 79.63 \pm 3.88$	[35]
18.	Ni/CaO-Al ₂ O ₃		Langmuir–Hinshelwood–Hougen–Watson (LHHW) model	480 - 888	$1.74 \times 10^7 \exp\left(\frac{-102065}{RT}\right)$	$E_{\text{CH}_4} = 102$ kJ/mol	[36]
19.	Ce _{0.70} La _{0.20} Ni _{0.10} O _{2-δ}		----	873 – 1023		$E_{\text{CH}_4} = 70.5$	[37]
20.	Ce _{0.70} La _{0.20} Ni _{0.10} O _{2-δ}		Power law	873 – 1023		$E_{\text{CH}_4} = 91.5$	[37]

2.5 Catalyst for dry reforming

To date, over ten different types of single metals and alloys have been reported for DRM reactions. The most frequently reported catalyst includes Ni, Pt, Co, and Rh. Table 2.2 provides summary of some recent findings from using these catalysts.

2.5.1 Nickel based catalyst

Nickel is the most utilized metal for dry reforming of methane because of its availability, strong reactivity, and cost efficiency when compared to noble metals. However, Ni-based catalysts are susceptible to deactivation due to carbon deposition and metal sintering. To enhance Ni's activity and stability, various strategies have been explored, including modifying support materials, optimizing preparation methods, and adding promoters [38], [39]. Significant research efforts have focused on designing catalysts that combine high activity with strong resistance to carbon deposition for the dry reforming of methane (DRM). Computational studies indicate that, under comparable particle size and dispersion, noble metals such as Ru and Rh exhibit superior catalytic performance compared to Ni. However, despite their enhanced activity and excellent resistance to coke formation, the limited availability and high cost of noble metals like Ru, Rh, and Pt restrict their large-scale application. As a result, Ni-based catalysts continue to dominate industrial DRM processes due to their affordability and performance. [40]. Table 2.3 shows a summary of recent findings carried out on DRM using Nickel based catalyst. Ni-based catalyst

Table 2.3: Recent findings on DRM using Nickel-based catalyst.

Catalyst	Reaction conditions	Preparation	Findings	Reference
Ni-VAP-H300 -	H ₂ atmosphere T = 400 - 800 °C	Introduction of strong metal-support interaction	A plausible strategy was achieved to boost the stability of the catalyst under extreme reaction conditions	[41]
Ni-La ₂ Ti ₂ O ₇ & Ni-Gd ₂ Ti ₂ O	T=800 °C T= 200 hours	Sol-gel method	The doping of the Gd and La enhanced the activation ability of CH ₄ with excellent stability over 200 hrs. Carbon deposition is also negligible.	[42]
Ni-La ₂ O ₃ -CeO ₂	T=400-800°C	Sol-gel method and wetness	The Ni-LaCe 1:4 and Ni-LaCe 1:1 catalyst shows high catalytic activity and stability in DRM test compared to Ni-C showed a lower carbon deposition which was attributed to the larger size of Ni-particles that was less effective.	[43]
Ni/Al ₂ O ₃	T= 700 °C P= 1am	One-pot evaporation-induced self-assembly	The catalyst system with Fe-doped (Fe/Ni ratio =0.5) exhibit high carbon deposition resistance with a log time stability of over 100 hr.	[44]
Ni-CeO ₂ -MgO	T= 1073 K P= 1 atm flowrate = 60 mL min ⁻¹	Co-precipitation	Addition of CeO ₂ to Ni-MgO influenced the type of carbon deposited promoting the growth of carbon nanotubes which stabilize the catalyst and minimize the formation of coke	[45]
HTNi-Y1.5	T=600 – 850 °C GHSV=20,000 mL.h ⁻¹ g ⁻¹ P=1 atm	Co-precipitation method	Carbon formation was minimized through controlled Ni crystallite size and modification of the catalyst with 1.5 wt % yttrium shows high conversion of CH ₄ and CO ₂ .	[46]
Ni/MgAl ₂ O ₄ Ni-K/MgAl ₂ O ₃	T=450 - 750 °C	Wet impregnation	Ni catalyst promoted with K perform excellently in inhibition of carbon deposition and hence have high coke resistant.	[47]

	P=1 atm CO ₂ :CH ₄ :N ₃ =1:1:3			
Ni/Zr Ni-Ce/Zr Ni _x Ce/LaZr	T=700 °C P=1 atm GHSV = 42,000 mL.h ⁻¹ g ⁻¹	Wet impregnation	Addition of lanthanum stabilized the zirconia support achieving an 80 % H ₂ yield and addition of ceria improves the dispersion of NiO, hence increasing H ₂ yield to 87 %	[48]
xNi/γ-Al ₂ O ₃ 5Ni/yMgAl 5Ni1Ce0.5La /30MgAl x-Ni loading y-MgO content	T=600 – 800°C P=1 atm GHSV=20,00 0-85,000 mL.h ⁻¹ g ⁻¹	Incipient wetness integration	Ce and La improved γ-Al ₂ O ₃ and MgO.Al ₂ O ₃ supported Ni catalysts' activity and stability. increased coke resistance and activity were noted at 5 wt% Ni and 30 wt% MgO, corresponding to SMSI	[49]
xK-Ni/Al ₂ O ₃ K- K ₂ CO ₃ x=0.5, 1, 2, 5 wt %	T= 800 °C P=1 atm GHSV= 36,000 mL.h ⁻¹ g ⁻¹ CH ₄ :CO ₂ :N ₂ = 1:1:2	Impregnation	The catalytic performance of Ni/Al ₂ O ₃ catalysts by modifying the catalyst with K ₂ CO ₃ . The modified catalyst exhibited high stability and the coke elimination reaction was demonstrated via transient experiment.	[50]
Ni/xLa-HAP, (x = 1, 3, 5, 7 wt%)	T= 750 °C P=1 atm GHSV= 24,000 mL.h ⁻¹ g ⁻¹ CH ₄ :CO ₂ = 1 :1	Co-precipitation	The Ni/xLa-HAP catalyst shown increased stability and conversion, while highest conversion of 73.2% of CH ₄ with an H ₂ /CO ratio of 0.84 at 750°C. The inclusion of La ₂ O ₃ led to enhance dispersion and carbon nanotubes that prolonged catalytic lifetime by protecting active nickel sites.	[51]
Ni-CaO-ZrO ₂	T=750 & 850 °C	Co-precipitation	The Ni-CaO-ZrO ₂ catalyst exhibits high anti-coking performance at 850°C due to unfavorable coking thermodynamics and small exposed Ni sizes, while at 750°C	[52]

	P= 1atm GHSV= 158,000 mL.h⁻¹g⁻¹ CH₄:CO₂ = 1. 2:1		more coking was observed despite kinetic inhibition by smaller Ni particles.	
La_{0.46}Sr_{0.34}Ti_{0.9}Ni_{0.1}O₃ (LSTN_{0.1})	T = 700 °C P=1atm GHSV= 26,400 mL.h⁻¹ g⁻¹ CH₄:CO₂ = 1. 2:1	Combustion	The Ni-doped perovskite show superior carbon-resistance for DRM compared to impregnated Ni and spinel NiAl ₂ O ₄ catalysts, showing no coke after 100 hours at 700 °C	[53]
Ni/Al₂O₃-F Ni/Al₂O₃-W Ni/Al₂O₃-S Where: F-Flower-like W-Wire-like S-Sphere-like	T=750 °C P=1atm WHSV= 26,400 mL.h⁻¹ g⁻¹ CH₄/CO₂/N₂ =3:3:4	Incipient wetness impregnation	The catalyst shows different performance on each support morphology. Ni/Al ₂ O ₃ -W showed high catalytic activity and coke resistance due to strong MSI while Ni/Al ₂ O ₃ -F shows high anti-coke properties but had lower initial catalytic activity due to fewer surface Ni active sites. Ni/Al ₂ O ₃ -S experienced acute carbon deposition and deactivation because of weak CO ₂ activation and larger Ni particles.	[54]

2.5.2 Method of preparation

Method of preparation is part of the major variable determining the catalyst structure, grain size, composition and catalyst dispersion during catalyst preparation. Hence, it influences coke resistance, catalyst stability and activity [55]. This section describes the various methods of preparation of Nickel based catalyst and their impacts on the Ni particle size, metal support reaction and their performance. These methods include sol-gel, one-pot, co-precipitation, plasma treatment, impregnation, ammonia evaporation and plasma treatment [56].

2.5.2.1 Sol-gel Method

The sol-gel (SG) preparation method is synthesized by preparing the gel using complexing agent and precursors. The sol-gel synthesis process begins by creating a gel from specific precursors and complexing agents. Followed by drying and pre-treatment of the gel to obtain the final catalyst. The inclusion of complexing agents is particularly beneficial in reducing Ni particle sintering, leading to smaller particle sizes and stronger metal-support interactions compared to conventional methods like impregnation [57]. The sol-gel technique has shown notable advantages in the preparation of multicomponent systems such as Co-Pt-Zr/Al₂O₃ and Co-Pt-Zr-La/Al₂O₃. These catalysts, which are produced with high dispersion and particle sizes mostly below 10 nm, incorporate metal oxides and micro alloys like Co-Pt bimetallic system and perovskite structures (e.g., LaCoO₃, LaAlO₃). When synthesized using a modified Pechini sol-gel method, they exhibit excellent catalytic activity, selectivity, and long-term stability in dry reforming, steam reforming, and combined CO₂-SRM processes. At reaction temperatures between 750 and 800 °C, they achieve nearly full methane conversion and create syngas with H₂/CO ratios ranging from 0.9 to 4.4 [58]. Additionally, the effectiveness of bimetallic (Ni-Fe) catalyst is enhanced by sol-gel

preparation method, with a particle size controlled by a shell factor. The catalyst exhibits optimum performance for DRM with high stability and activity [59].

In another findings, Ni-Co/ Al_2O_3 -MgO-ZrO₂ nano-catalyst, which is used to produce syngas from CO₂-reforming of CH₄, has attributes and performance that are much improved by the sol-gel process. Two zirconia precursors were tested: zirconyl nitrate hydrate (ZnH) and zirconyl nitrate solution (ZNS). The catalyst prepared with ZNS (referred to as NCAMZ-ZNS) was analyzed using XRD, FESEM, EDX, BET, and FTIR. These analyses revealed that the nano-catalyst possessed excellent physiochemical properties, such as a suitable crystalline structure, homogeneous active phase dispersion, uniform morphology, smaller average particle size (15.7 nm), and increased surface area. Notably, this catalyst achieved stable syngas production with an H₂/CO ratio close to 1 and sustained high conversions of CH₄ (97.2%) and CO₂ (99%) at 850 °C over a 1440-minute test [60]. Furthermore, SBA-15 mesoporous silica synthesized using a modified sol-gel process exhibited a highly ordered pore structure with a narrow distribution (~7.8 nm) and a high surface area of 834 m²/g. This allowed for uniform Ni dispersion and optimal metal loading. Ni/SBA-15 catalysts showed excellent performance in DRM, especially under isothermal conditions with a CH₄/CO₂ ratio of 1.5:1, across 550–700 °C [61]. Similarly, Nd₂O₃-promoted Ni-based catalysts supported on Al_2O_3 -Y₂O₃ (x = 0–4% Nd₂O₃), synthesized via sol-gel, demonstrated superior DRM performance. Notably, Ni/ Al_2O_3 -Y₂O₃-3%Nd₂O₃ achieved outstanding activity and coke resistance at 800 °C, attributed to its high Ni dispersion, improved basicity, and abundant oxygen vacancies. These features minimized Ni agglomeration and carbon deposition, confirming the sol-gel method's effectiveness in enhancing structural and catalytic stability for DRM [62].

2.5.2.2 Co-Precipitation

Precipitation has been a promising synthesis method for the preparation of Ni-based catalyst, with their properties tunable by controlling parameters such as temperature, pH, or rate evaporation. This approach adopts the concepts of nucleation and growth to achieve a controlled precipitation from a precursor solution. The idea behind this process, is "burst nucleation," which is crucial for precipitation as well as the production of colloids and can be used to impregnate catalyst. When multiple metal cations are uniformly distributed and co-precipitated from a homogeneous solution, the process is specifically termed coprecipitation [63]. Co-precipitation is often known as the low supersaturation approach. During catalyst synthesis, it is possible to quickly solidify the homogenous distribution of several metal cations in a mixed solution into a catalyst precursor by appropriately adjusting the precipitation parameters. In contrast to the widely utilized impregnation techniques for pre-formed supports, these materials incorporate both the precursor species and the active components within the same material [55].

A range of synthesis techniques have been applied in the preparation of catalysts for DRM. In a recent study, [64] evaluated the performance of Ni-based catalysts supported on $\text{La}_2\text{Ce}_2\text{O}_7$, synthesized via co-precipitation, sol–gel, and glycine nitrate combustion methods. Among these, the co-precipitated catalyst demonstrated the highest stability and activity, attributed to enhanced metal–support interaction and the dynamic modulation of particle size, which improved oxygen vacancy formation, surface area, and pore structure. In another study, [65] developed a trimetallic catalyst system (Co–Ni–Pd/CaO) doped with La_2O_3 using a surfactant-assisted co-precipitation technique. This catalyst achieved CH_4 and CO_2 conversions of 84% and 92%, respectively, under a 1:1 CH_4 : CO_2 feed ratio. Similarly, [66] adopted a one-step co-precipitation method

to synthesize Ni–Ir/MgAl(O) hydrotalcite-derived catalysts for pressurized DRM. The resulting material displayed excellent resistance to carbon deposition due to the formation of well-dispersed, small Ni particles and enhanced structural stability. Contrarily, [67] investigated how titration rate during co-precipitation affects catalyst performance. They found that faster titration led to smaller Ni crystallites and better dispersion in Ni–MgO catalysts, while the addition of CeO₂ further enhanced oxygen storage capacity. The Ni–MgO–CeO₂ catalyst prepared under rapid titration showed optimal performance when tested at 800 °C and a GHSV of 720,000 mL·g⁻¹·h⁻¹ [67]

2.5.2.3 Impregnation

In the impregnation method, metal particles are introduced onto the support by contacting the support with a metal precursor solution. Two primary impregnation techniques are commonly employed: incipient wetness impregnation, where the volume of the impregnating solution is equal to the pore volume of the support, and conventional wet impregnation, in which the solvent volume exceeds that of the support. The conventional method often leads to greater metal dispersion, as the excess solvent facilitates deeper penetration and more uniform distribution of metal ions. In contrast, incipient wetness impregnation tends to produce less dispersed metal particles, since the limited solvent volume restricts diffusion within the pore network during the impregnation process [56]. According to the findings of [68], Ni-Al₂O₃ catalyst was synthesized via impregnation by varying the calcination temperatures. The stability test reveals the catalyst produced at calcination temperature at 700 °C exhibited optimum catalyst performance with minimal carbon deposition on its surface. Additionally, wetness impregnation method significantly enhances the properties and performance of Ni-based catalyst systems for hydrogen production from DRM [69]. Ceria-promoted Ni catalysts supported on lanthanum–zirconia (5Ni_xCe/LaZr; x = 0–5 wt.%) were

synthesized via the wetness impregnation method. Notably, the catalyst with 2.5 wt.% ceria-promoted catalyst (5Ni2.5Ce/LaZr) exhibited remarkable high thermal stability, excellent CH₄ decomposition, efficient CO₂ interaction, and over 87% hydrogen yield [48].

Furthermore, as revealed by [49] the coke deposition behavior of catalysts in DRM reaction was greatly affected by the incipient wetness impregnation approach. Utilizing the incipient wetness impregnation procedure, a range of catalysts including Ce and La promoters, varying MgO content (30–70 wt%) in a MgO–Al₂O₃ matrix, and Ni loadings ranging from 5 to 12.5 wt% supported on γ -Al₂O₃. Among these, the formulation containing 5 wt% Ni and 30 wt% MgO exhibited superior activity and resistance to coking at 800 °C, 1 atm, with a CH₄/CO₂ ratio of 1 and GHSV of 1700 h⁻¹. This performance was attributed to the formation of a stable MgAl₂O₄ spinel structure rich in medium-strength basic sites and enhanced metal–support interaction [49]. Figure 2.7 presents a comparative summary of different catalyst synthesis methods, along with representative stability test results for each approach.

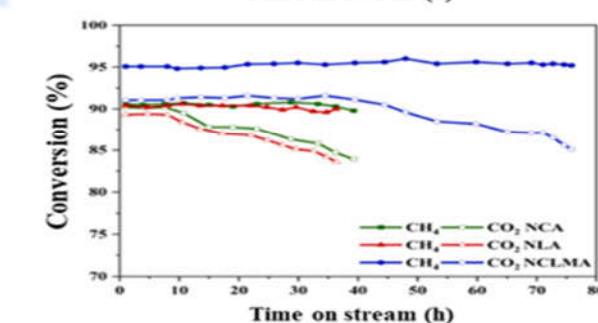
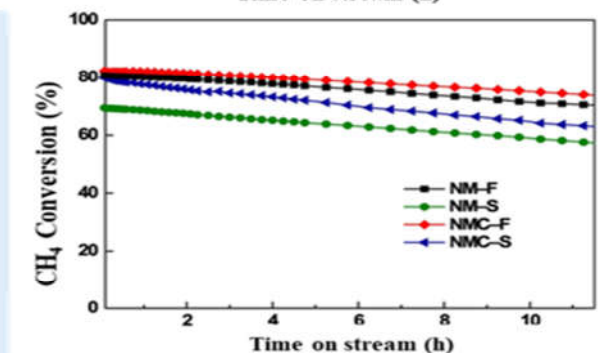
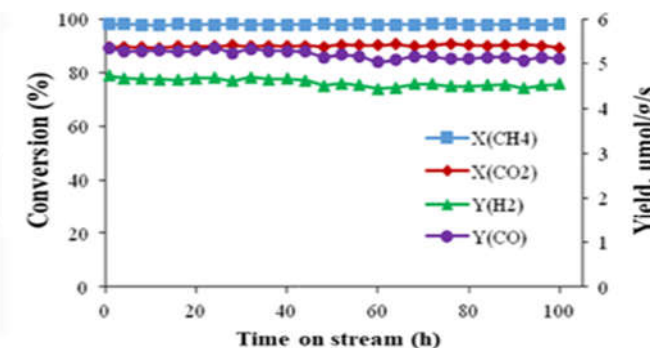
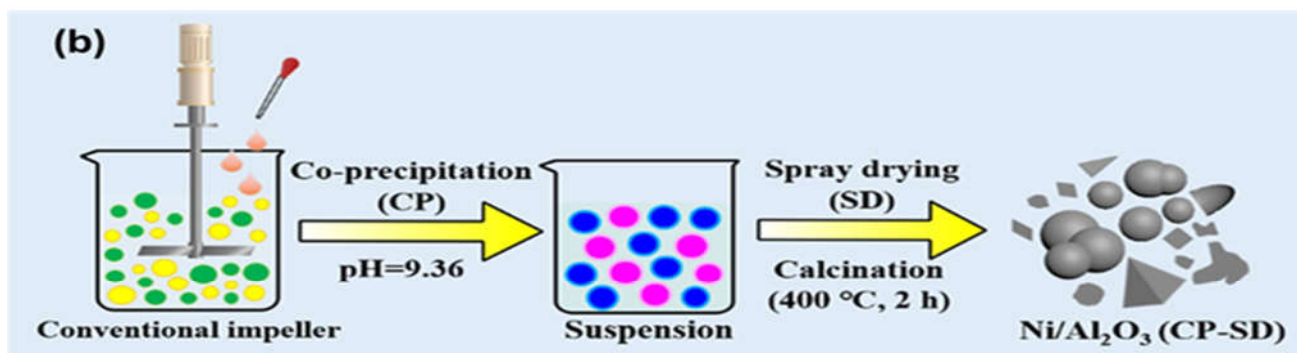
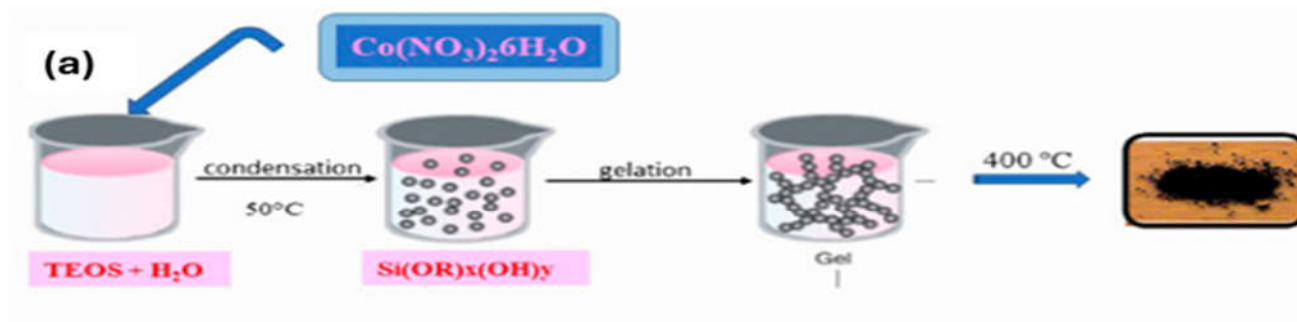


Figure 2.7: Different catalyst synthesis method (a) Sol-gel method adapted from [70] (b) Co-precipitation [67] (c) Impregnation[49].

2.6 Core shell structure catalyst synthesis for DRM

The catalytic reforming of methane into hydrogen has gained considerable attention over the past few decades, particularly as a strategy to reduce CO₂ emissions from direct methane combustion. Among the various catalyst morphologies explored for dry reforming of methane (DRM), recent studies have highlighted the effectiveness of core-shell catalyst structures. Notably, Ni-based core-shell systems have demonstrated improved catalytic activity, enhanced thermal stability, and superior resistance to carbon deposition under DRM conditions [71]. The concept of core-shell materials was first introduced in the 1990s, originally to describe semiconductor systems with a concentric structure where a central core is enclosed by one or more surrounding layers or "shells." In catalysis, this idea has been adapted to describe materials in which the active phase (core) is encapsulated by a protective or functional outer layer (shell). These structures can include single- or multi-shell architectures and even hollow microspheres or microcapsules, offering additional versatility in tuning catalyst behavior for demanding reactions such as DRM [72].

2.6.1 Structural types of the core-shell catalyst

Core-shell catalysts can be categorized into several structural types based on the configuration of their core and shell components. The most common designs include mono core-shell, multi-shell core-shell (also known as sandwiched structures), multi-core-shell, sandwiched multi-core-shell, and yolk-shell (or rattle-type nanoparticles). Figure 2.8 illustrates these structural classifications. These architectures are typically described using the notation A@B, where "A" represents the core and "B" the shell, signifying that material A is enclosed within material B. Each configuration offers distinct advantages in terms of stability, diffusion control, and active site accessibility,

making them suitable for tailoring catalyst behavior under specific reaction conditions like DRM.[71], [72].

2.6.1.1 Single-and multi-core-shells

The most common type of core-shell catalyst is the single core-shell which typically consists of a core encapsulated on a shell. This shell is virtually always porous in catalysis to facilitate the movement of reacting species to the core and the release of products from the core [73]. From recent studies [7], [74] who adopted the single core shell catalyst system, this configuration enhances the metal support interaction, high dispersion and maintain improved stability of the active core when compared with the conventional catalyst configuration. Alternatively, multi-cores can be encapsulated on a single shell resulting in a core with high surface area and a large interfacial area between the core and the shell per unit volume. In some instances, multi-core-shell catalysts are easier to synthesize using techniques akin to those employed in the conventional catalyst preparation. This can be verified from [75] procedure where the Ni@SiO₂ core-shell catalyst requires the synthesis of Ni nanoparticles prior to encapsulating the shell while a one-pot reverse micelle approach has been demonstrated to be effective in synthesis of multi-Ni@SiO₂ catalyst.

2.6.1.2 Yolk@shell and multi-core@hollow structures

Hollow or yolk-shell structures are typically created via soft or hard templating techniques, in which a hollow area is created by first coating a sacrificial template layer—such as carbon or silica—between the shell and core and then removing it. For DRM, several yolk-shell catalysts have been described, including hollow-NiPt@SiO₂ [76], hollow-Ni@SiO₂ [77] Ni@Ni phyllosilicate@SiO₂ [78] and Ni@NiPhy@CeO₂ [79]. Using a simple precipitation process, hollow spherical catalysts with a multi-Ni-

core@Niphylosilicate@CeO₂ structure (Ni@NiPhy@CeO₂) were synthesized and evaluated against a similar system lacking the outer CeO₂ shell (Ni@NiPhy). In the context of DRM, the CeO₂-containing catalyst exhibited excellent resistance to carbon deposition even at relatively low temperatures (600 °C) and performed well under high gas hourly space velocities (GHSV), reaching 1880 L·g⁻¹·h⁻¹ at 700 °C. Under standard GHSV conditions (36 L·g⁻¹·h⁻¹), this catalyst maintained stable CH₄ and CO₂ conversions of 72.8% and 79.1%, respectively [79]. Despite these promising results, comprehensive studies that directly compare yolk-shell and core-shell catalyst structures under identical operating conditions remain limited. One noted drawback of the yolk-shell architecture is the limited interaction between the core and shell due to the hollow gap between them. This spatial separation may reduce synergistic effects, such as bifunctional catalysis and CO₂ activation by the support, when compared to conventional core-shell systems [73].

2.6.1.3. Sandwiched multi-core-shell

One emerging advancement in core-shell catalyst design is the development of multi-core-shell architectures with sandwiched structures. In this configuration, multiple active metal cores are embedded between two shell layers, which may be composed of identical or different materials [74], [80]. This design enables each core to interface with distinct materials, allowing the combination of different functionalities within a single catalyst. As a result, these sandwich-like systems offer greater flexibility in tailoring catalyst properties compared to conventional core-shell structures. A notable example is the tri-layer system reported by Wang et al. (2022) [74], where CeO₂ was used as the inner layer to provide oxygen storage capacity, while Ni nanoparticles were dispersed on the surface of a silica sphere. In addition to enhanced functionality, this

structure offers simplified synthesis routes. Unlike traditional core-shell methods which often involve complex, multi-step procedures such as colloidal synthesis and shell coating for each nanoparticle the sandwiched multi-core-shell design can be fabricated using more scalable techniques like sol-gel, precipitation, or hydrothermal methods. Nonetheless, for these emerging architectures to be adopted at a commercial scale, comprehensive techno-economic evaluations are essential to assess their feasibility, scalability, and cost-effectiveness relative to existing catalyst designs [81], [82], [83].

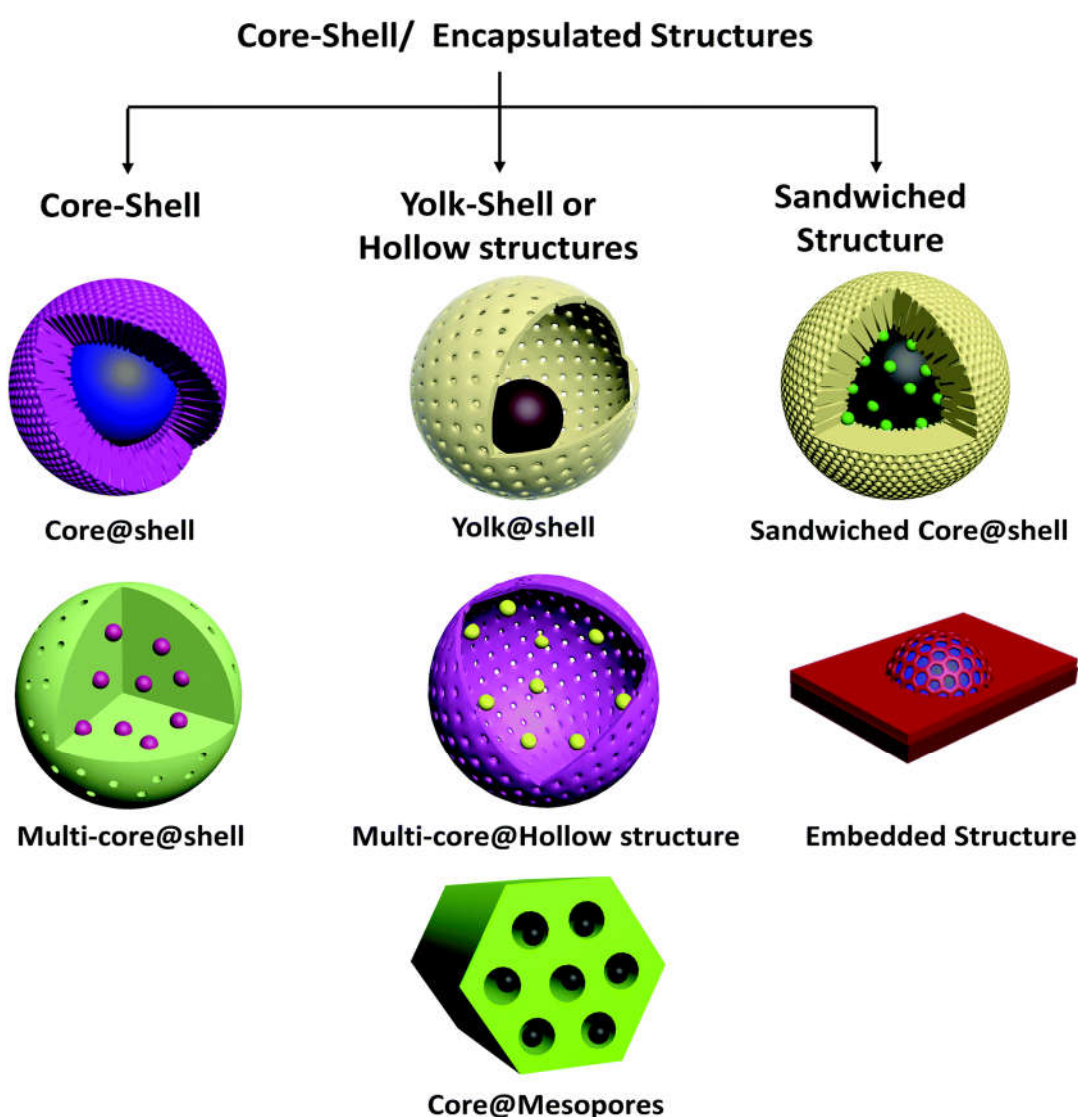


Figure 2.8: Structural Classification of the core-shell catalyst [73].

2.6.2 Influence of core-shell catalyst on DRM

Core-shell catalyst architectures, when carefully engineered, have demonstrated the ability to enhance essential catalytic properties and surpass the performance of traditional catalyst systems. The aim of designing a core-shell catalyst is to elevate the efficiency and stability of traditional catalysts. Selecting an appropriate support material introduce bi-functional characteristics and to optimize this effect the need for encapsulating the catalyst can maximize this benefit. However, unlike conventional catalyst preparation, the synthesis of core-shell systems is often more complex, resource-intensive, and involves additional process. Although they might have better performance, their practical use needs to be justified by thorough techno-economic studies because of their higher manufacturing costs and dependability issues. Improved production techniques and greater trust in these catalysts could result from early achievements. The following enhanced factors could be achieved from coating of the catalyst. Table 2.4 presents a comparative overview of recent research on core-shell catalyst structures and their impact on catalytic activity, stability, and coke resistance in DRM.

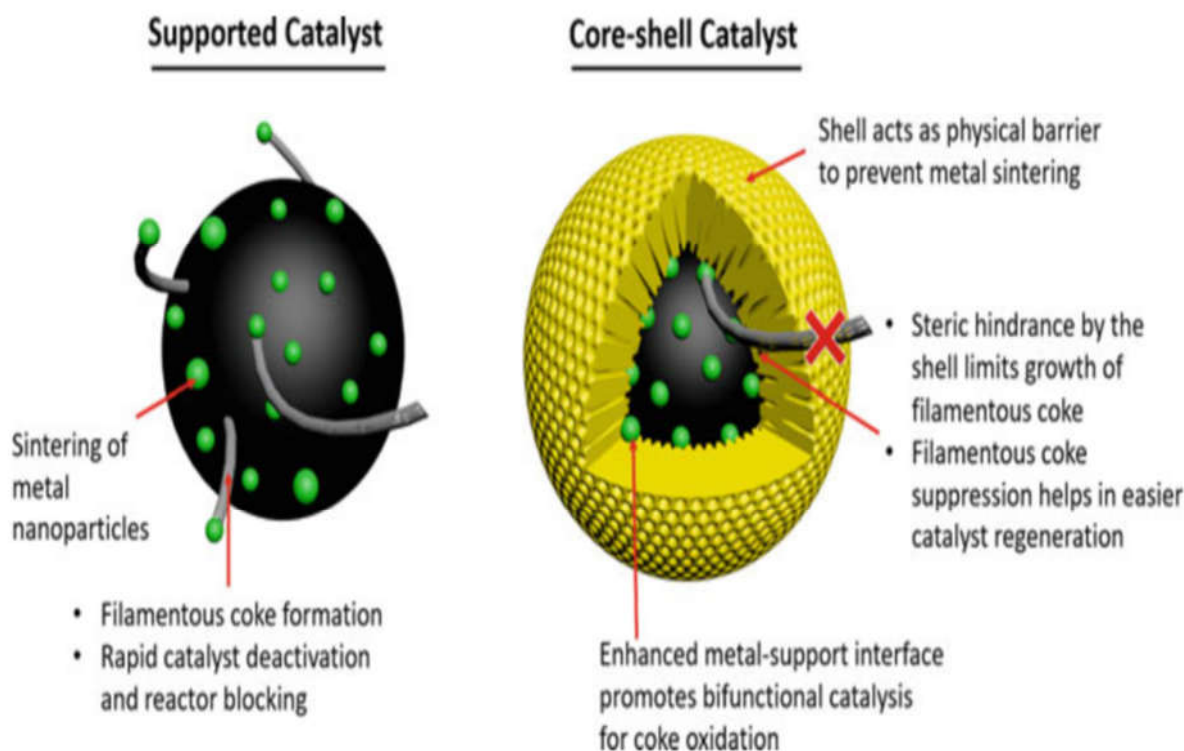


Figure 2.9: Comparative advantages of core-shell catalysts versus conventional supported catalysts in CO₂ reforming. [83].

2.6.2.1 Bifunctional Catalysis

Core-shell architectures allow the integration of multiple active catalytic sites within a single structure, enabling the design of systems that facilitate tandem or sequential reactions. By tailoring the core and shell components to target specific reaction steps, complementary transformations can occur more efficiently. Unlike traditional bifunctional catalysts, where active sites are randomly dispersed and operate in an unstructured environment, core-shell systems offer a more controlled spatial arrangement, improving selectivity and reaction coordination. In a study by Das et al., [84], a bifunctional catalyst composed of NiCo-MgAl@CeO₂ was synthesized for DRM. The structure consisted of a Mg-Al hydroxide core enclosed by a CeO₂ shell. The shell's lattice oxygen played a crucial role in enhancing activity and mitigating

deactivation by oxidizing H_2S , thereby reducing sulfur poisoning. The addition of cobalt in the core further delayed deactivation by modifying the sulfur chemisorption kinetics. Figure 2.10b presents O_2 -TPD profiles, showing the evolution of reactive lattice oxygen from CeO_2 . This oxygen species reacts at the core-shell interface, facilitating CO/CO_2 formation and inhibiting coke accumulation. Additionally, H_2 -TPR analysis (Figure 2.10a) reveals that the CeO_2 -encapsulated catalyst exhibits a lower reduction temperature (670–680 °C) compared to the unencapsulated form, indicating improved reducibility and more energy-efficient activation [84].

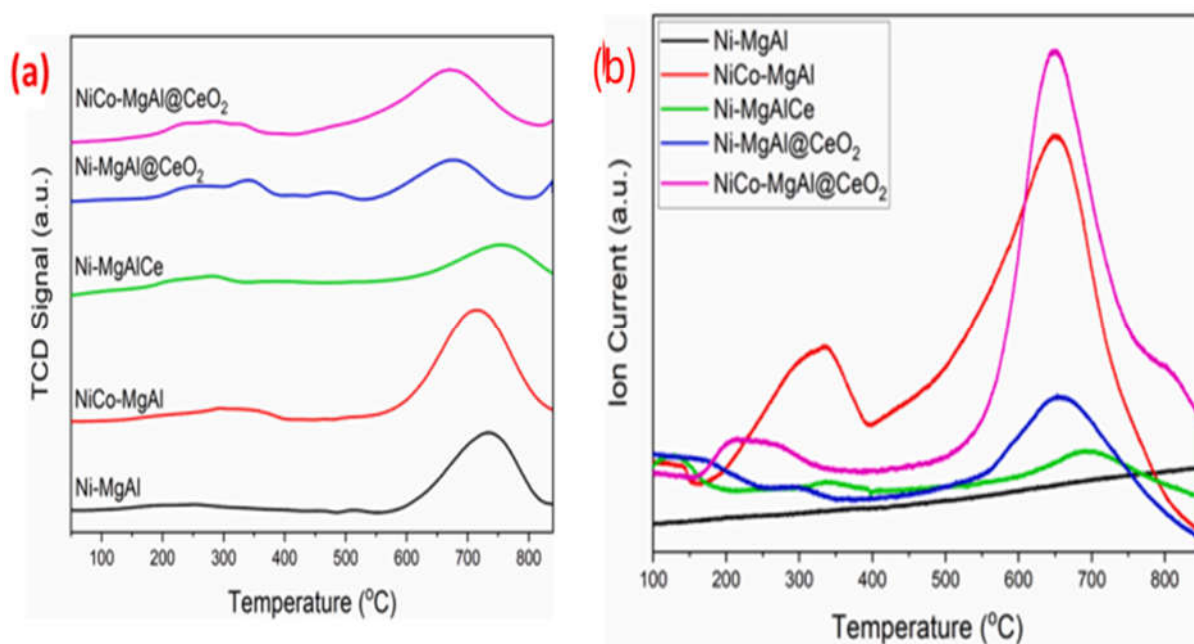


Figure 2.10: (a) H_2 -TPR, and (c) O_2 -TPD profiles of catalysts [84].

Table 2.4: Effect of Core shell catalyst synthesis for DRM

Catalyst system	Reaction conditions	Encapsulation method	Method of Preparation	Findings (Mechanism – CH ₄ , CO ₂ activation, anti-coking; connect it with the properties)	Ref.
NSLF-x (x = 3 to 15 wt%)	T= 700 °C, P=1atm; WHSV=60,00 mL/g-h;	Microemulsion approach	Wet impregnation	The presence of basic sites in SLF aids the activation of CH ₄ and CO ₂ by improving the adsorption and promoting DRM. The unique morphology and structure of the NSLF-x catalyst aids the thermal stability and minimizes coke resistance.	[85]
5wt%Ni/CeO ₂ –ZrO ₂ @SiO ₂	T=400 – 600 °C P=1atm GHSV=12,000 – 24,000 mLg ⁻¹ h ⁻¹	Structure-oriented method (CTAB and TEOS)	Impregnation	The core-shell structure catalyst does not only improve the conversion of CH ₄ /CO ₂ and the yield of H ₂ /CO in the photothermal synergistic DRM but enhanced light absorption, inhibition of carbon deposition and resistance to sintering (by preventing nanoparticle migration).	[86]
10 wt%Ni-SiO ₂ @SiO ₂	T= 500 – 700 °C P=1atm GHSV=24,000 mLg ⁻¹ h ⁻¹	Structure-oriented method	Precipitation	The increase in thickness of the catalyst coating by varying the amount of TEOS results in low carbon formation and prevents agglomeration of metal particles. Increase in coating time also leads to negligible amount of deposited carbon and increase in catalytic activity.	[87]
xNi-SiO ₂ @SiO ₂ (2.5 – 15 %)	T= 500 – 700 °C P=1atm GHSV=12,000-36,000 mLg ⁻¹ h ⁻¹	Stober method	Impregnation	The best catalytic activity was recorded at 10 % Nickel loading. When compared with the conventional 10Ni/SiO ₂ the encapsulated catalyst displays higher active sites with strong MSI that results in minimum coke formation and anti-sintering.	[88]
xNi/WGSG (0.99, 3.10 and 3.59 %)	T=600 – 900 °C P=0.1MPa GHSV = 1000 h ⁻¹	-	One-pot impregnation	The catalyst with medium Ni loading (i.e. 3.1 wt%) shows higher catalytic performance with better anti-cooking and anti-sintering activities.	[89]

Ni-SiO₂@Ce_{0.8}M_{0.2}O_{2-δ} (M = Fe, Co, Ni)	T= 550 – 650 °C, m = 200 mg, F _{CH₄/Ar} = 30 Ncm ³ /min (5% CH ₄ /Ar), F _{Ar} = 50 Ncm ³ /min.	Improved Stober method		The tri-layer structure provides enhanced redox activity, oxygen storage capacity and contributes to the selective oxidation of CH ₄ in CL-DRM. High activity is recorded for Ni- phyllosilicate@Ce _{0.8} Fe _{0.2} O _{2-δ}	[74]
In _x Ni@SiO ₂ (x=0.1,0.5,1,3 and 7 wt.%)	T=550 -800 °C, WHSV = 18,000 mLg ⁻¹ h ⁻¹ , P=1atm, CH ₄ :CO ₂ =1:1	One-pot method	Wet impregna tion	Confined indium-nickel metallic alloy nano catalyst (InNi@SiO ₂) showed superior coking resistance and stability for DRM which is because of the synergy between In and Ni.	[7]
NiCo@SiO ₂	T=800 °C, GHSV = 300 Lgm ⁻¹ h ⁻¹ CH ₄ :CO ₂ :N ₂ =1:1: 1	Microemulsio n method	Precipitat ion	The core shell structure provides a close synergy interaction between the Ni and Co which leads to high activation and adsorption of CH ₄ . A confined environment is created by SiO ₂ for the activation of CO ₂ ; hence it inhibits coke deposition by promoting CO ₂ to CO conversion. Additionally, the catalyst system ensures a controlled size which eventually increases the catalytic activity and surface area.	[90]
Ni,Co/SiO ₂ and Ni/SiO ₂ &Co	T=750 °C, WHSV = 36,000 mLg ⁻¹ h ⁻¹ CH ₄ :CO ₂ :N ₂ =1:1: 1	Sol-gel microencapsu lation	Impregna tion	The presence of Co in the catalyst system aids the reduction of coke formation and metal sintering due to its high affinity towards CO ₂ . Additionally, SiC formation during DRM reaction results in self-cleaning of the active sites and hence maintains high catalyst stability. Ni-Co encapsulation in the core of silica microsphere contributes to the catalyst anti-coking properties by decreasing the migration of active materials and carbon nucleation on the active sites.	[91]

2.6.2.2 Resistance to Sintering and Coking:

Metal sintering is one of the primary deactivation pathways for catalysts during DRM, as it reduces the available active surface area and promotes the growth of whisker-type carbon structures, which can physically disrupt the catalyst framework. The extent of carbon accumulation resulting from CH_4 or CO_2 dissociation is highly influenced by the size of metal nanoparticles. Kim et al. [92] reported that Ni particles supported on alumina aerogel must reach a critical diameter of approximately 7 nm to initiate the growth of filamentous carbon during DRM. This process involves the diffusion of surface carbon into the Ni lattice, forming a nickel carbide intermediate, which subsequently leads to the growth of carbon nanotubes (CNTs) catalyzed by metallic Ni. However, CNTs with small diameters tend to be thermodynamically unstable, making smaller Ni nanoparticles more resistant to carbon filament growth under DRM conditions. Therefore, controlling metal particle dispersion and minimizing aggregation during the reaction is essential for preserving catalyst integrity and ensuring long-term stability [73].

In the last decade, extensive efforts have been devoted to designing thermally stable core-shell catalysts for dry reforming of methane (DRM). Among these, Metal@ SiO_2 -type structures have been widely explored, with mesoporous silica frequently employed as a protective shell. Its high thermal resistance, tunable pore size, large surface area, and ease of synthesis make it an ideal encapsulating material. The porosity and shell thickness can be precisely tailored by modifying variables such as the concentration of silica precursors, hydrolysis duration, and the type of surfactant used during synthesis. Numerous studies have highlighted the effectiveness of silica-encapsulated Ni-based catalysts for DRM [7], [86], [90], [93]. While nickel is known for its high catalytic

activity in DRM, it also promotes carbon deposition, especially when supported on SiO₂ or Al₂O₃, leading to gradual deactivation. In contrast, Ni@SiO₂ catalysts have demonstrated stable performance with minimal coke formation, even during extended operation of up to 100 hours. These catalysts are typically synthesized by encapsulating pre-formed NiO particles or surfactant-stabilized Ni nanoparticles within a mesoporous silica shell, often using sol–gel or one-pot microemulsion techniques.

From Bian & Kwai, findings, they synthesize a multi-core shell catalyst which was encapsulated on a silica shell (silica@Ni@silic). This novel catalyst system shows a stable CO₂ conversion of 60 % for DRM at an optimal temperature of 600 °C. Furthermore, from the TEM analysis (Figure 2.11 a,b and c) of the spent encapsulated catalyst show almost no coke formation was observed by comparing with the unencapsulated catalyst (NiPS). Also from the TGA analysis (Figure 2.11d), no clear peaks indicates carbon formation for NiPS@silica-0.4 and NiPS@silica-0.6, with only slight weight losses of 7.6% and 5.1%, respectively (Bian & Kawi, 2018). In another findings, Zhao et al., synthesize NiCo@SiO₂ catalyst by carrying the shell thickness. From the TG analysis (Figure 2.11e), for Ni@SiO₂-3, Ni@SiO₂-5 and Ni@SiO₂-10 catalyst, the TG profile exhibits no significant carbon formation but on increasing the shell thickness to 60 nm, Ni@SiO₂-60 showed high weight loss of about 60 % from 550 °C to 780 °C. On the other hand, TEM image of Ni@SiO₂-5 (Figure 2.11f) indicates the morphology of the catalyst has been maintained with no structural damage while Figure 2.11g show that the Ni-nanoparticles are covered by a thick film of the shell, hence it reduced accessibility of the active sites due to the thick cells [90]. Kaviani et al., 2022 [93] synthesize Ni-SiO₂@SiO₂ catalyst by using the ammonia evaporated method followed by the encapsulation. From H₂-TPR analysis of the catalysts (Figure 2.11h) the silica shell in the encapsulated catalyst significantly

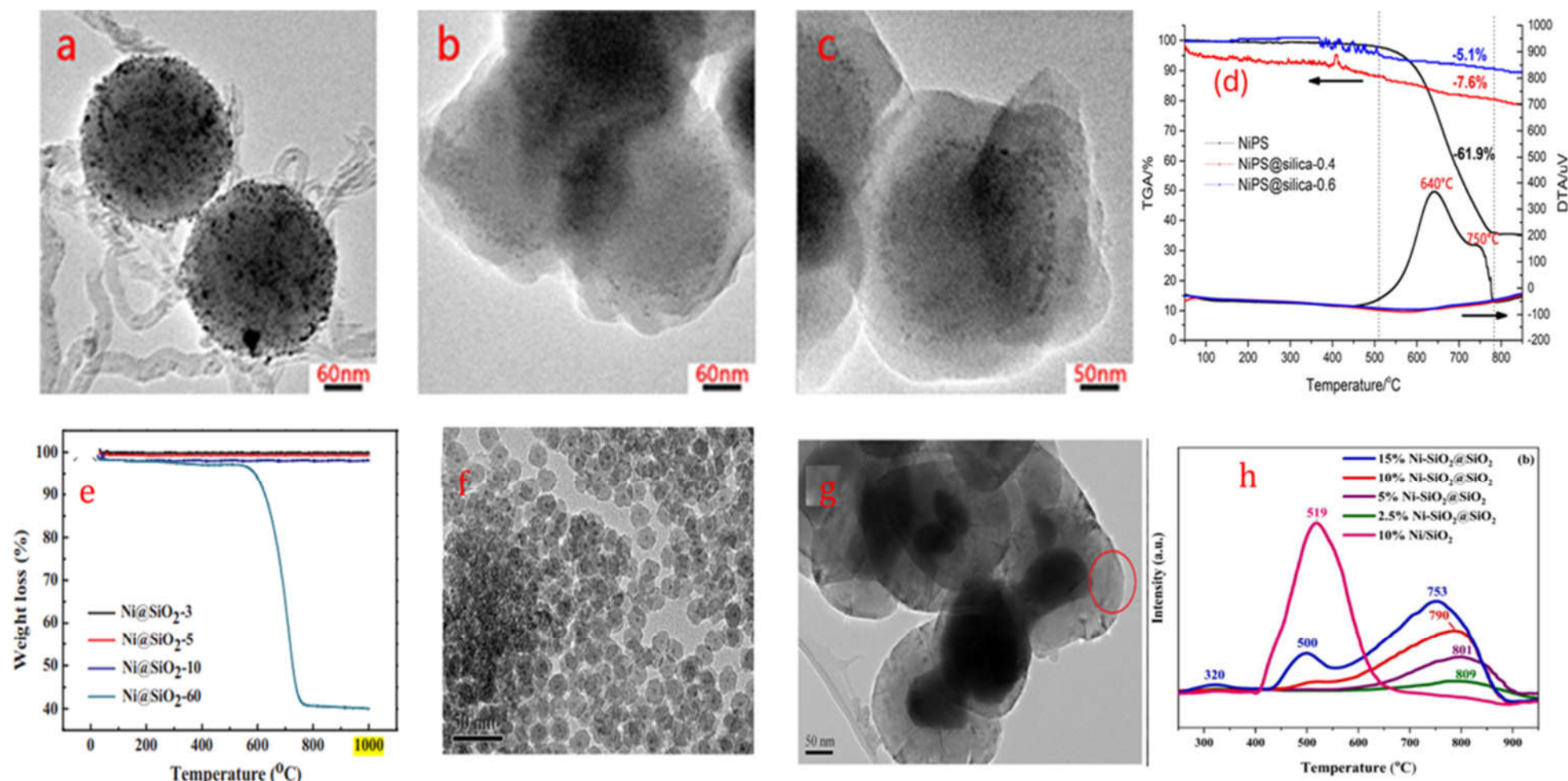


Figure 2.11: (a–c) TEM images of spent catalysts after DRM testing: (a) NiPS, (b) NiPS@silica-0.4, (c) NiPS@silica-0.6 (d) TGA–DTA measurements of the spent catalysts after catalytic tests (Bian & Kawi, 2018). (e) TGA patterns of Ni@SiO₂ (f) TEM image of Ni@SiO₂-5, (g) TEM image of Ni@SiO₂-60, [90] (h) H₂-TPR profiles of the xNi-SiO₂@SiO₂ (x = 2.5 to 15 wt%) and 10Ni/SiO₂ catalyst [93].

influences the catalyst performance by the reducibility of Ni. The interaction between the silica shell and Ni-core makes the reduction temperature increase as observed from the shift of the broad peak in comparison to the unencapsulated catalysts.

2.6.2.3 Catalyst activation (CO₂ and CH₄ activation) and stability

The core-shell structure offers a process of fine-tuning catalyst properties by combining different materials with complementary features. Hence, the catalyst can perform multiple functions in comparison to the conventional catalyst with no encapsulation. This catalyst can improve CH₄ and CO₂ activation through the active sites, enhance oxidation, and reduce coke formation in DRM. A similar configuration is when a support material is coated onto metal nanoparticles to create a core-shell catalyst. This does not only improve the stability of the catalyst but also enhances the activation of CH₄ and CO₂ at the active sites.

From Liu et al., 2018 findings, a novel core-shell catalyst with Ni-ZrO₂ as the core and SiO₂ as the shell (represented as Ni-ZrO₂@SiO₂) was prepared by adopting the one-pot facile strategy. The catalyst shows no coke formation and high stability (240 h) when subjected to CH₄ and CO₂ feed at 800 °C. This was visibly confirmed by the active Ni particles well distributed in the silica shell after 20h and subsequently after 240 h (Figure 2.12a&b). From comparison of CO₂ adsorption with Ni-ZrO₂@SiO₂, Ni-ZrO₂/SiO₂, and > Ni@SiO₂; Ni-ZrO₂@SiO₂ exhibit the highest adsorption of CO₂ as shown in CO₂-TPD analysis profile, Figure 2.12c. This Implies that CO₂ can easily access the Ni active sites and the Ni core is not blocked by the SiO₂ [94]

In another means to improve the efficiency of DRM Ni@S-1@SiO₂ dual shell catalyst was synthesized. The catalyst encased Ni particles on S-1 surface within a mesoporous silica shell which limits the mobility of Ni-particles and prevents oxidation of active sites. The catalytic stability test results show that the initial activity of both catalysts at 650 °C is nearly identical. However, for the Ni@S-1@SiO₂ catalyst, CH₄ and CO₂ conversions remain consistent throughout the 25-hour reaction period. In contrast, the Ni@S-1 catalyst exhibits a 24.1% drop in methane conversion (from 61.7% to 37.6%) after 11 hours of reaction (Figure 2.12d&e). These findings suggest that the bilayer-confined Ni@S-1@SiO₂ catalyst demonstrates strong stability under conditions most susceptible to carbon deposition, emphasizing the benefits of its unique dual-core-shell structure. Moreover, extended stability tests reveal that after 50 hours of DRM reaction at 650 °C, the bilayer-confined catalyst continues to maintain excellent stability with only a minor decline in activity [95]. Additionally, Han et al, [96] synthesize Ni/ZSM-5 catalyst encapsulated on a silica shell via the sol-gel method. The spatial encapsulation improves the catalyst's resistance to coking and shows high activity compared to the encapsulated catalyst (Fig. 2.12f).

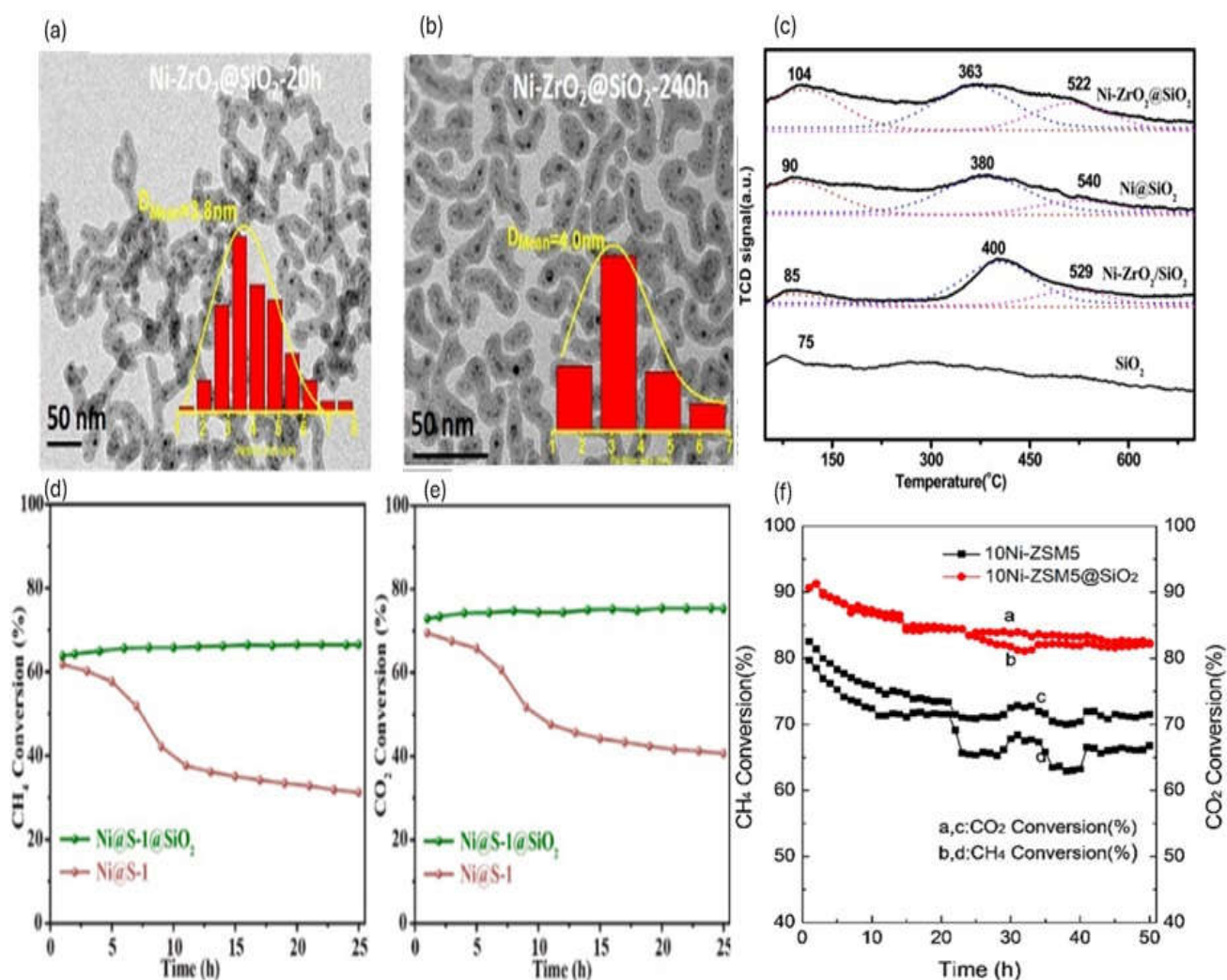


Figure 2.12: TEM images and Ni particle size distributions of the spent (a) Ni-ZrO₂@SiO₂-20 h, (b) Ni-ZrO₂@SiO₂-240 h catalysts (c) CO₂-TPD profiles of freshly reduced Ni-ZrO₂@SiO₂, Ni@SiO₂, Ni-ZrO₂/SiO₂ catalysts, and SiO₂ support [94]. Catalytic stability test results of the catalysts over 25 h. (d) CH₄ conversion and (e) CO₂ conversion. Reaction conditions: 650 °C, CH₄: CO₂ = 1:1, WHSV = 18,000 mL g_{cat}⁻¹ h⁻¹, p = 1 atm [95]. (f) Conversion of catalysts reaction for 50 h [96].

CHAPTER 3

METHODOLOGY

3.1 Materials

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (97.0 wt%), NH_4OH solution (28-30 wt%), Tetraethyl orthosilicate (TEOS) (98.0 wt%), $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99 %), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%), were all obtained from Sigma-Aldrich. Cetyltrimethylammonium bromide (99%), and ethanol (99.0%) were purchased from Merck chemicals and Ammonium bicarbonate from J.T Baker chemicals. All reagents used were analytical grades. De-ionized water was prepared in the lab using Bioevopeak Water Purifier LWP-F3-30DUV

3.2 Catalyst synthesis

Three catalyst supports were synthesized, impregnated on a nickel precursor and then finally encapsulated on silica by using the structured-oriented method. The following procedures were adopted.

The $\text{CaO-Al}_2\text{O}_3$ support was prepared by first decomposing CaCO_3 in a furnace at 900 °C with a heating rate of 10 °C/min. CaO powder was then treated with aluminum nitrate nonahydrate and the resulting paste was dried overnight at 100 °C. Following this procedure, the solid was then calcined at 600 °C for 10 hrs at a heating rate of 10 °C/min. The Nickel precursor was further impregnated to the support and then calcined at 750 °C for 14 h to get rid of HNO_3 and improve the metal support interaction and produce the $x\text{Ni}/\text{CaO-Al}_2\text{O}_3$, where x is the weight fraction of the Ni present.

For the second catalyst set, CeO-Al₂O₃ support was prepared via hydrolysis. This was achieved by dissolving Ce(NO₃)₃·6H₂O and Al₂O₃·3H₂O in a 100 ml distilled water, followed by steady heating of the mixture at 60 °C while stirring at 400 rpm for 5 h to promote thorough mixing. After hydrolysis, the mixture was transferred into an oven and dried overnight at 100 °C to remove water content. The support was then further calcined at 750 °C for 14 hrs to ensure stability and high metal support interaction to achieve. This was followed by the impregnation of the Nickel precursors and then calcined at 750 °C for 14 h to produce xNi/CeO-Al₂O₃ catalyst.

The Ce-Zr support was prepared using the sol-gel method by dissolving cerium and zirconium precursors 1:1 into 300 ml of distilled water. The solution was mixed and stirred to obtain a homogeneous solution. This was followed by the addition of (NH₄)₂CO₃ solution as the hydrolyzer which aids the gel formation. Constant stirring was maintained throughout the addition of the hydrolyser to maintain uniform gel formation. The resulting gel was placed in an oven at 60 °C for ageing for 24 h and further raised the temperature to 100 °C for another 24 h. The gel was then emptied into a crucible for thermal treatment and ramped calcination. The ramped calcination involved initial heating at 150 °C for 10 h, followed by increasing the temperature to 200 °C for another 10h and finally increasing the temperature to 750 °C for another 10 h and finally cooled to room temperature. This was followed by impregnation of Nickel catalyst as mentioned above to achieve xNi/Ce-Zr catalyst

Finally, the core-shell catalyst of each catalyst set was prepared using the structured oriented method. TEOS was used as the SiO₂ source and CTAB as the template agent. The following step was adopted by modifying Tengfei et al. method [86]. CTAB was dissolved

in de-ionized water, ethanol and ammonium hydroxide with molar ratio 1:10:150:275. A specific quantity of the catalyst ($x\text{Ni}/\text{CaO-Al}_2\text{O}_3$, $x\text{Ni}/\text{CeO-Al}_2\text{O}_3$ and $x\text{Ni}/\text{Ce-Zr}$) was then dispersed into the solution and TEOS was added dropwise, maintaining a molar ratio of 1.5:1.0 for TEOS to CTAB. The resulting mixture was then dried at 100 °C overnight. The powder is then calcined at 750 °C for 5 h to get our final silica encapsulated catalyst.

3.3 Catalyst characterization

3.3.1 Temperature program reduction (TPR)

The process of temperature programmed reduction (TPR) was meticulously conducted utilizing the highly sophisticated Micromeritics Autochem 2920 apparatus, which is notably endowed with an advanced thermal conductivity detector that facilitates precise measurements. For the TPR experiment, approximately 40 mg of the catalyst was carefully placed into the U-shaped reactor, where it underwent an oxidation process over the course of one hour at an elevated temperature of 750 °C, utilizing a gaseous mixture composed of 5% oxygen complemented by an inert helium atmosphere. Subsequently, a gaseous mixture comprising 10% hydrogen, which was balanced with helium to optimize reaction conditions, was introduced at a regulated flow rate of 50 cm³ per minute, while the reactor temperature was gradually elevated from ambient conditions to a peak of 1000 °C at a consistent rate of 10 K per minute. Following the completion of this temperature elevation phase, the catalyst was permitted to return to ambient temperature, thereby completing the reduction process under carefully monitored conditions. The meticulous control of both temperature and gas composition during the TPR experiment is critical for elucidating the catalytic properties and behaviour of the material under investigation.

3.3.2 Ammonia temperature program desorption (TPD)

Micromeritics' Autochem II 2920 analyzer was used to perform the ammonia TPD. About 100 mg of the catalyst was encased within a U-shaped quartz tube reactor, which was subsequently placed into the sample port. Initially, the sample underwent reduction in a flow of 10% hydrogen in helium at a temperature of 500 °C, followed by a two-hour degassing process under argon at the same thermal conditions. The temperature was then adjusted to 120 °C, followed by saturation with ammonia (i.e. ~5.5% NH₃ balanced with helium) flowing at the rate of 50 ml/min for one hour. A sensitive thermal conductivity detector then monitored the ammonia desorption while the system was ramped up to 600 °C at a rate of 10 °C per minute.

3.3.3 X-ray diffraction

The analytical methodology known as X-ray diffraction (XRD), which is a highly sophisticated and widely employed technique in the field of materials science and crystallography, was meticulously applied to investigate the intricate and detailed crystalline structure of the catalyst under examination, utilizing a state-of-the-art Rigaku Miniflex diffractometer that was precisely calibrated and set to operate at a voltage of 40 kV and a current of 20 mA. The XRD was conducted at 2 θ angle from 10° to 80°, at a scanning at a rate of 2° per minute, and data was recorded at intervals of 0.02°. Furthermore, the data collected during this experimental procedure was cross-referenced and interpreted in conjunction with the extensive database provided by the Joint Committee on Powder Diffraction Standards (commonly referred to as JCPDS), which was instrumental in facilitating the identification and characterization of the various phases present within the catalyst material being studied.

3.3.4 Thermal gravimetric analysis

An SDT Q600 analyzer was used to study the thermal behavior of the used catalysts of both the encapsulated and unencapsulated catalyst under air. 0.005 g of each catalyst was taken and placed in the crucible for the thermal gravimetric measurements. The furnace temperature was then raised from room temperature ($\sim 25\text{ }^{\circ}\text{C}$) to $900\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. Weight- and differential weight measurements were taken and reported in the results/discussion section.

3.3.5 Raman spectroscopy

Thermo-Fisher Scientific's DXR3 Raman spectrometer having a CCD detector, was used to investigate the nature of the carbon formed on the used catalyst. The carbon peaks were compared with that of carbon nano tubes (CNTs)

3.3.6 Brunauer Emmett Teller (BET) Surface Area Analysis

The specific surface area and pore structure of the catalysts were determined using Microtrac's BELSORP MAX X-114 analyzer. Prior to analysis, each sample was degassed under vacuum at $300\text{ }^{\circ}\text{C}$ for 2 hours to remove adsorbed impurities. Nitrogen adsorption-desorption isotherms were recorded at liquid nitrogen temperature ($-196\text{ }^{\circ}\text{C}$), and the surface area was calculated using the BET method, while pore volume and average pore diameter were obtained via the Barrett Joyner Halenda (BJH) method.

3.3.7 Scanning Electron Microscopy (SEM)

The surface morphology and elemental composition of the catalysts were examined using a JEOL 5800LV SEM equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector. The instrument operates with a tungsten filament and supports a voltage of up to

30 kV. Imaging was performed in both secondary and backscattered electron modes to observe surface features and microstructural contrasts. EDS analysis was used to identify and quantify elemental distributions across selected regions of the catalyst samples.

3.3.8 Transmission Electron Microscopy (TEM)

High-resolution imaging of the catalyst microstructure was performed using a JEM-2100F Field Emission Transmission Electron Microscope (FE-TEM) operating at an accelerating voltage of 200 kV. The instrument is equipped with a field emission gun, enabling atomic scale imaging with a lattice resolution of 0.14 nm. TEM was used to examine morphology and dispersion of Ni nanoparticles of the catalyst.

CHAPTER 4

CATALYST EVALUATION - Ni/Ce-Al₂O₃ & Ni/Ce-Al₂O₃@SiO₂

4.1 Introduction

This chapter presents the characterization and performance evaluation of Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ for dry reforming of methane (DRM). The incorporation of Ce is intended to enhance redox properties and oxygen mobility, while silica encapsulation is explored as a strategy to improve catalyst activity, thermal stability and coke resistance.

4.2. Fresh catalyst characterization

The crystalline structure of the freshly synthesized catalysts was investigated via XRD.

Figure 4.1: XRD pattern of Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ shows the XRD patterns for Ni/Ce-Al₂O₃ and the silica-encapsulated variant (i.e., Ni/Ce-Al₂O₃@SiO₂) for 2θ angle ranging from 10°-80°. The two catalysts give a similar XRD pattern.

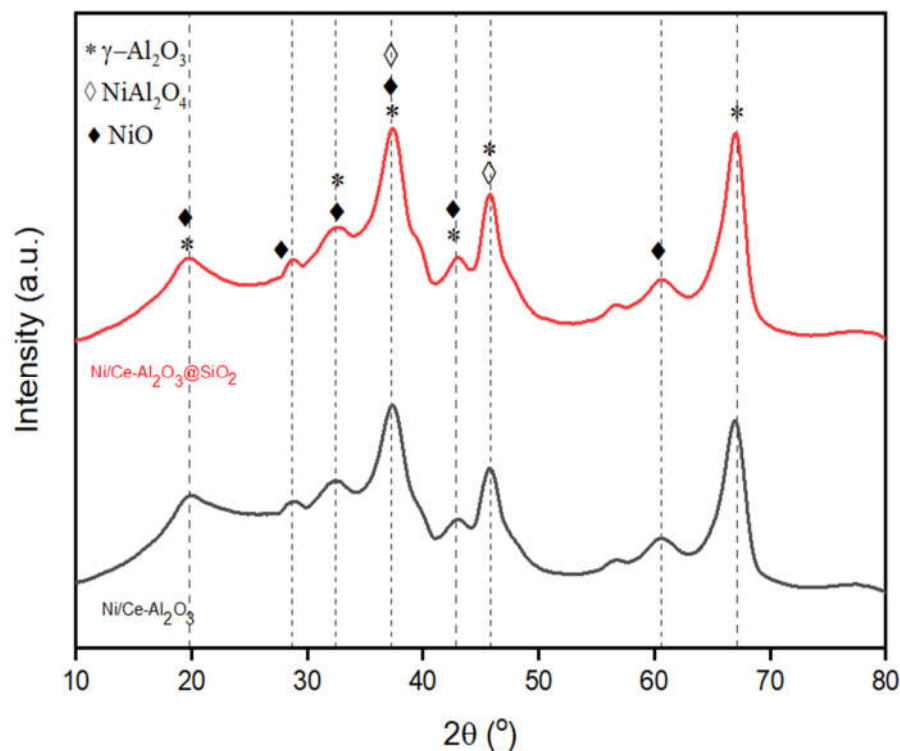


Figure 4.1: XRD pattern of Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂

The X-ray diffraction patterns reveal the characteristics of NiO, γ -Al₂O₃, and NiAl₂O₄ as revealed by the JCPDS database. Prominent Al₂O₃ peaks were observed at around $2\theta = 32.7^\circ, 37.35^\circ, 45.75^\circ$, and 67.8° (JCPDS: 00-004-0875) for both catalysts. The NiO phase is discernible at 2θ values of $37.3^\circ, 43.3^\circ$, and 63.0° , which correspond to the (111), (200), and (311) crystallographic planes, respectively, as per the standards outlined in JCPDS: 01-078-0643 and confirmed from other findings [97], [98]. Notably, the peaks observed at $2\theta = 45.5^\circ$ indicate the presence of the spinel, NiAl₂O₄ (ref. JCPDS: 01-078-1601) a robust metal support, a phenomenon that is not only advantageous but also essential for ensuring the prolonged operational life and stability of the catalyst, particularly when subjected to the demanding and often rigorous conditions characteristic of dry reforming of methane (DRM) [97], [99]. Due to the small amount of CeO₂ it was difficult to ascertain its

corresponding peaks. Additionally, the silica encapsulation does not significantly affect the crystalline phases, suggesting that the encapsulated catalyst retains the structural integrity of the original material.

Figure 4.2 illustrates the H₂-TPR profiles of the synthesized catalyst samples. Two peaks are prominent for Ni/Ce-Al₂O₃ catalyst at 408 and 821 °C for Ni/Ce-Al₂O₃, which shift to ~512 and 848°C upon SiO₂ encapsulation (i.e. Ni/Ce-Al₂O₃@SiO₂).

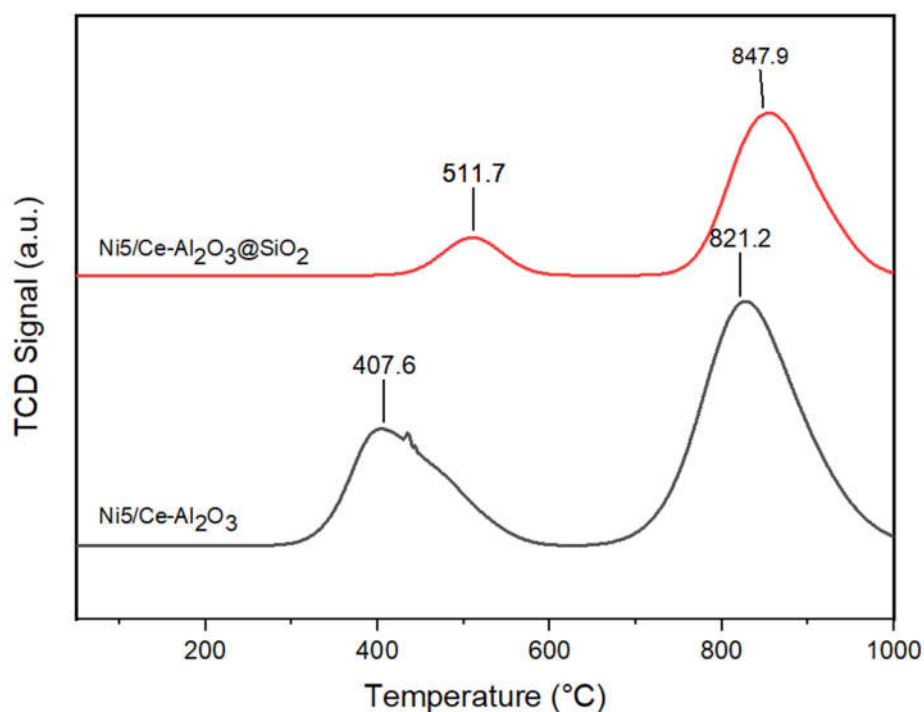


Figure 4.2: H₂-TPR Profile of fresh Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂

The low-temperature reduction peaks indicate the reduction of moderately bound NiO species to the Ce-Al₂O₃ support [29]. These species tend to be reduced easily with lower activation energy providing active metallic Ni species for initiating DRM reaction. The high-temperature peaks are attributed to the reduction of strongly bound Ni species, such as

NiAl₂O₄ spinel or Ni bounded with CeO₂–Al₂O₃ supports, which require higher activation energy [19]. The shift of the reduction peaks after SiO₂ encapsulation denotes the confinement effects on the Ni species, as well as the stronger metal support interaction in the encapsulated catalyst.

The acidic characteristics of the catalyst are determined through the application of NH₃-TPD measurements (See Figure 4.3). Three peaks are shown in the TPD profiles. The low temperature peaks (100-200 °C) represent the weak acid sites, moderate temperature peaks (200-400 °C) represent the moderate acidic sites and higher temperature peaks (above 400 °C) represent the strong acid sites. For both catalysts, the weak site peak has higher intensity as compared to the moderate and high acidic sites. The total acidity calculated was 0.00137 mmol/g for Ni/Ce-Al₂O₃ and slightly lower 0.00116 mmol/g for Ni/Ce-Al₂O₃@SiO₂.

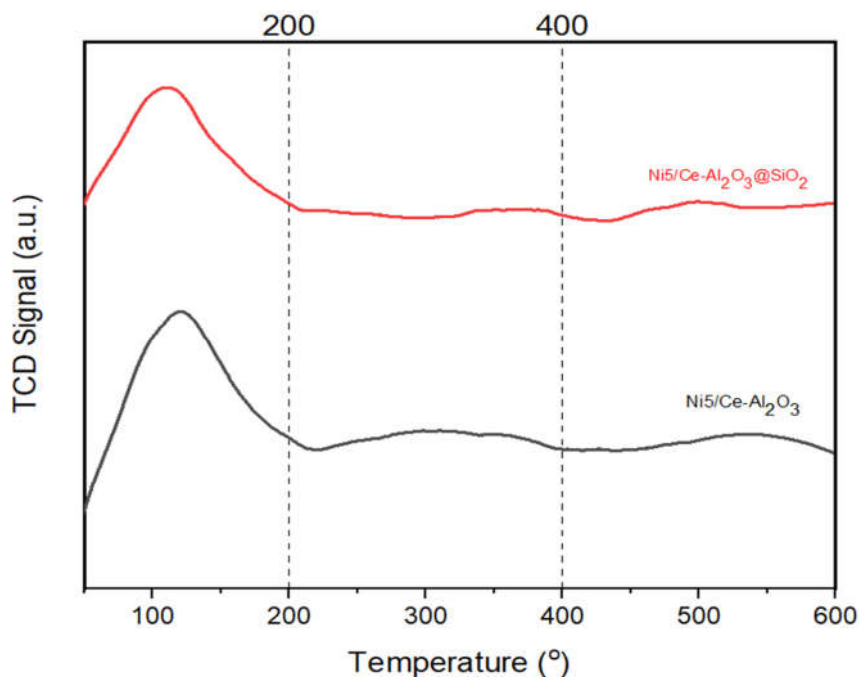


Figure 4.3: NH₃-TPD of the fresh catalyst

Additionally, the CO₂-TPD analysis (Figure 4.4) highlights a clear enhancement in surface basicity following SiO₂ encapsulation. The silica shell not only stabilizes the Ni/Ce-Al₂O₃ but also improves its CO₂ activation capacity. While the bare catalyst exhibited two desorption peaks corresponding to weak (~ 101 °C, 5.32×10^{-5} mmol/g) and strong (~ 601 °C, 8.39×10^{-4} mmol/g) basic sites. On the other hand, Ni/Ce-Al₂O₃@SiO₂ catalyst displayed three peaks including a significantly broader and more intense high-temperature desorption at ~ 614 °C with a total uptake of 1.60×10^{-3} mmol/g, nearly double that of Ni/Ce-Al₂O₃. This increase indicates a higher density of strong basic sites, likely resulting from enhanced Ni dispersion and stabilization of surface oxygen species within the SiO₂ shell. These findings align with NH₃-TPD analysis, which showed a slight reduction in strong acid site intensity Ni/Ce-Al₂O₃@SiO₂. This shift suggests that SiO₂ encapsulation creates a surface with higher basicity but moderated acidity, an ideal balance that promotes

efficient CO₂ adsorption, minimizes side reactions, and contributes to the superior DRM performance and stability observed for the encapsulated catalyst.

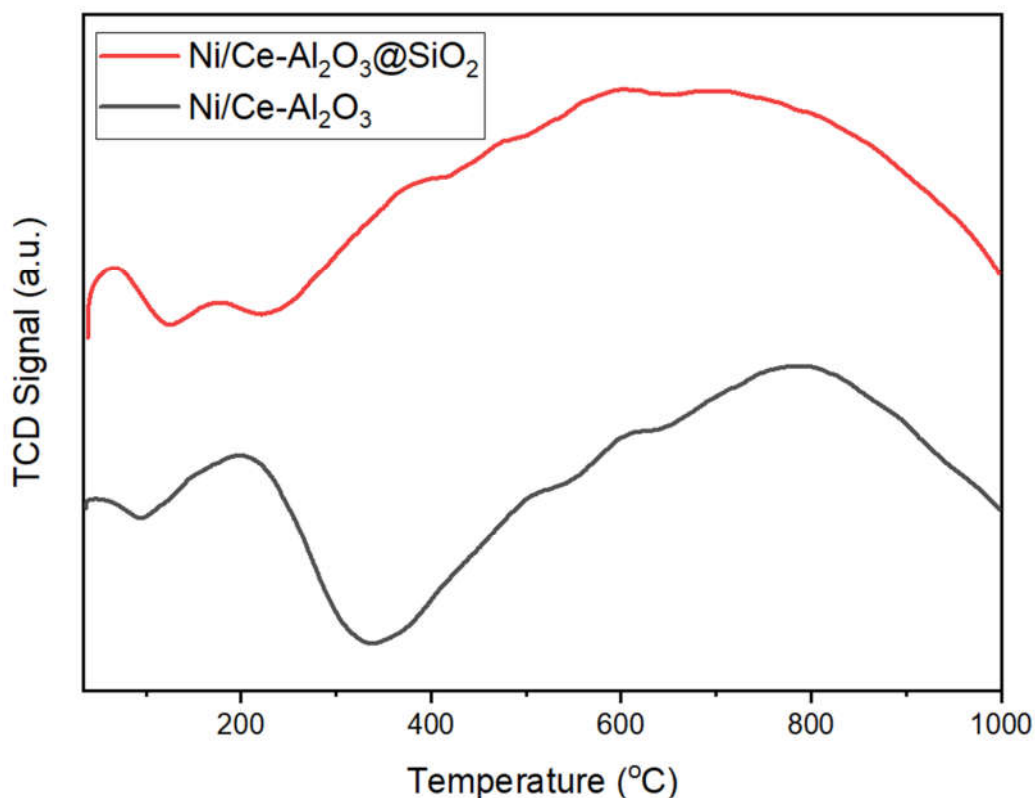


Figure 4.4: CO₂-TPD of the fresh catalyst

The nitrogen adsorption–desorption isotherms for Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ catalysts are shown in Figure 4.5. Both catalysts exhibit type IV isotherms with H3-type hysteresis loops, characteristic of mesoporous materials. However, after encapsulating the catalyst with silica, a noticeable improvement in textural properties is observed. As shown in Table 1, the Ni/Ce-Al₂O₃ catalyst have a surface area of 97.11 m²/g, with a total pore volume of 0.3011 cm³/g and an average pore diameter of 6.20 nm. However, Ni/Ce-Al₂O₃@SiO₂ exhibit a higher surface area, reaching 222.68 m²/g, alongside an increase in pore volume to 0.4554 cm³/g. At the same time, the average pore diameter slightly

decreases to 4.09 nm. These changes point to the role of the silica shell in introducing additional porosity and enhancing the overall surface area available for catalysis. The smaller pore diameter in the Ni/Ce-Al₂O₃@SiO₂ suggests the formation of more confined mesopores, which could influence how molecules diffuse through the structure. Meanwhile, the higher surface area provides a greater number of active sites for nickel dispersion, potentially improving catalytic efficiency during DRM.

Table 4.1: Textural Properties of Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ Catalysts

Catalyst	Surface Area (m ² /g)	Total Pore Volume (cm ³ g ⁻¹)	Average pore diameter (nm)
Ni/Ce-Al ₂ O ₃	97.11	0.3011	6.2014
Ni/Ce-Al ₂ O ₃ @SiO ₂	222.68	0.4554	4.0898

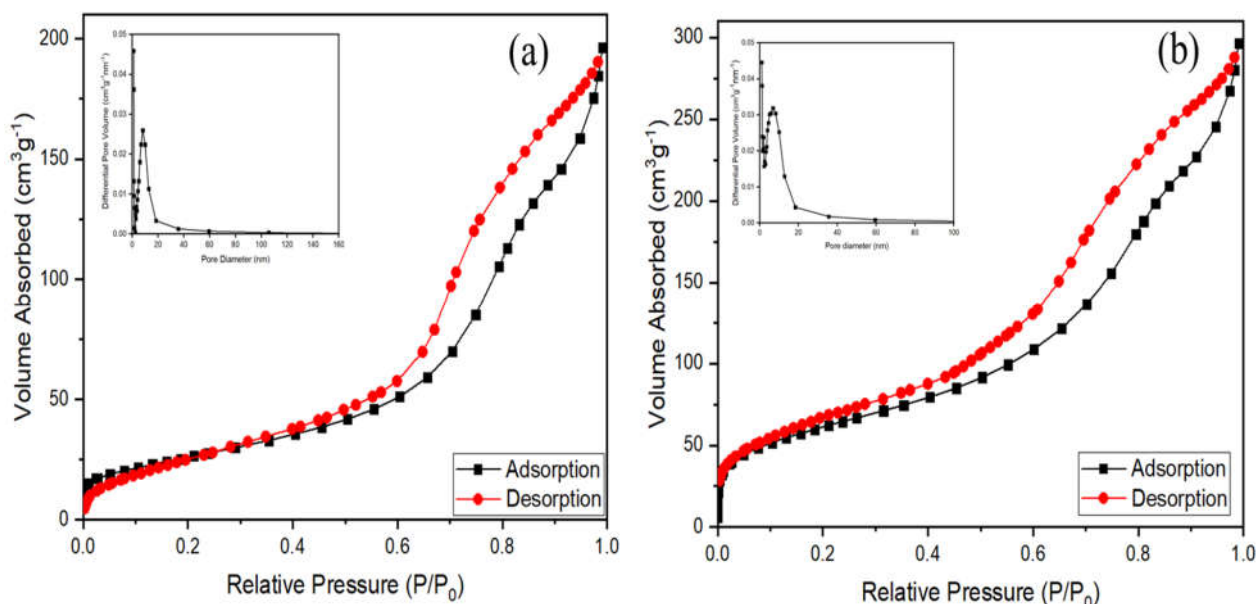


Figure 4.5: BET Analysis of the fresh catalyst

To corroborate these findings, CO chemisorption analysis was employed to probe the dispersion and accessible metallic surface area of Ni species as shown in Table 4.2. The encapsulated catalyst demonstrated a higher metal dispersion (14.51%) and larger metallic surface area (4.83 m²/g) compared to the unencapsulated pair (13.95% dispersion and 4.64 m²/g metallic surface area), indicating that the silica shell contributes to maintaining smaller and more dispersed Ni particles. This is consistent with the slightly smaller particle diameter which suggests that SiO₂ encapsulation inhibits particle agglomeration, preserving active surface sites under DRM conditions.

Table 4.2: Surface and Structural Properties of Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ via CO Chemisorption

Catalyst	Ni Dispersion (%)	Ni Surface Area (m ² /g sample)	Ni Surface Area (m ² /g metal)	Particle diameter (nm)
Ni/Ce-Al ₂ O ₃	13.95	4.64	92.87	7.26
Ni/Ce-Al ₂ O ₃ @SiO ₂	14.51	4.83	96.60	6.98

Figure 4.6 illustrates the scanning electron microscopy (SEM) images of the catalyst samples, providing significant insights into their morphological characteristics and textural attributes. Figure 4.6a shows the morphology of Ni/Ce-Al₂O₃, while Figure 4.6b represents Ni/Ce-Al₂O₃@SiO₂. The images reveal a range of particle sizes, spanning from nanoscale to microscale and macroscale. The particles observed at the nanoscale and microscale levels are presumably associated with Ni and/or NiO species, while certain nanoscale particles may be attributed to CeO₂. Conversely, the particles classified as macroscale are primarily associated with Al₂O₃. This analysis was further validated from the energy-

dispersive spectroscopy (EDS) mapping represented in Figure 4.6c,d, which details how elements are distributed among the samples. In **Error! Reference source not found.b**, the presence of microspheres is particularly prominent, most likely attributable to the encapsulation effect of SiO₂ on the catalyst. This observation is substantiated by the EDS mapping, which accentuates the occurrence and dispersion of Ni, Al, and Si. Nevertheless, owing to the minimal concentration of CeO₂ within the catalyst, it was undetectable at the specified magnification for Ni/Ce-Al₂O₃@SiO₂.

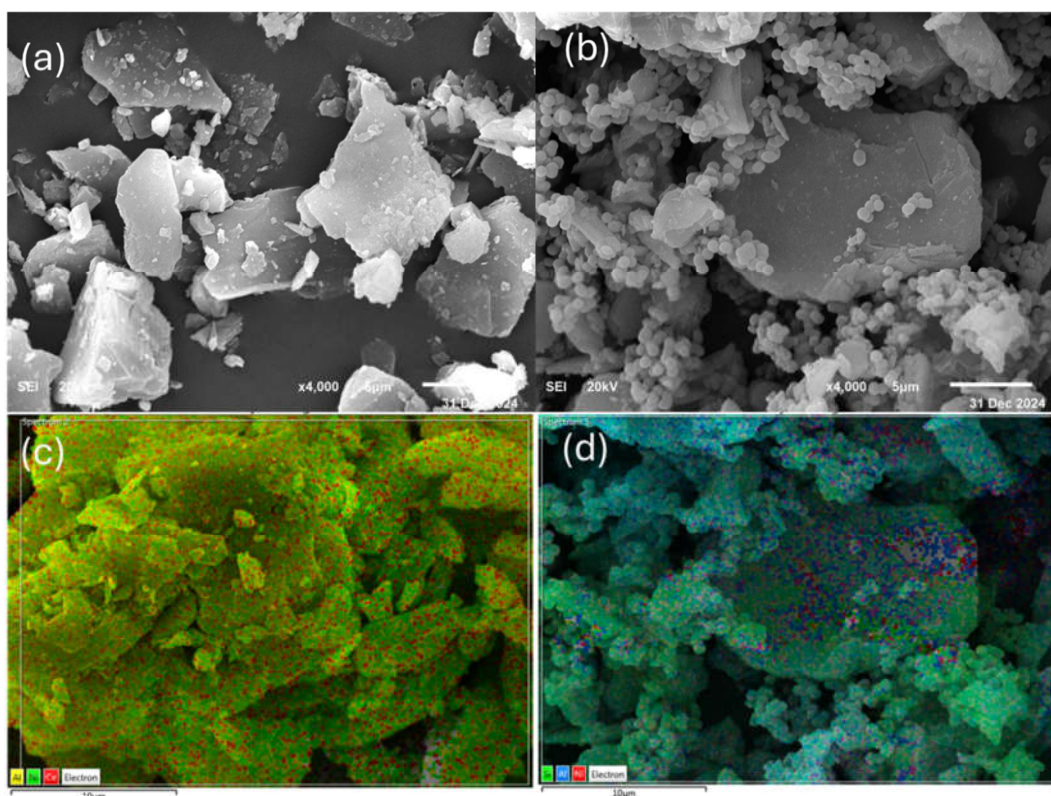


Figure 4.6: SEM images of fresh catalyst (a) Ni/Ce-Al₂O₃ (b) Ni/Ce-Al₂O₃@SiO₂ (c) EDS-Mapping Ni/Ce-Al₂O₃ (d) EDS-Mapping Ni/Ce-Al₂O₃@SiO₂

The TEM images for the fresh catalysts, Ni/Ce-Al₂O₃ (Figures a–c) and Ni/Ce-Al₂O₃@SiO₂ (Figure 4.7 d–f), reveal notable differences in particle dispersion and

structural characteristics. For the Ni/Ce-Al₂O₃ catalyst (Figure 4.7a–c), the nickel particles appear less uniformly distributed. At a magnification of 10 nm (Figure 4.7 c), considerable agglomeration of Ni particles is detected, resulting in the formation of larger conglomerates. This phenomenon can be ascribed to diminished metal-support interactions and restricted stabilization conferred by the Ce-Al₂O₃ support. Conversely, the Ni/Ce-Al₂O₃@SiO₂ catalyst (Figure 4.7d–f) demonstrates a markedly superior dispersion of Ni particles at the identical magnification (10 nm, Figure 4.7f). This augmented dispersion is a direct consequence of the encapsulating SiO₂ layer, which stabilizes the particles and inhibits agglomeration. At the 100 nm magnification (Figure 4.7e), robust SiO₂ layers enveloping the nickel particles are distinctly observable. These layers function as a protective barrier, affording structural integrity and shielding the Ni particles from sintering. On the other hand, the Ni/Ce-Al₂O₃ catalyst (Figure 4.7b) lacks such encapsulation, leaving the Ni particles directly exposed on the Ce-Al₂O₃ support. The encapsulation effect discerned in the Ni/Ce-Al₂O₃@SiO₂ catalyst is anticipated to enhance its efficacy by mitigating particle sintering, improving dispersion, and augmenting resistance to carbon deposition during the reaction. These structural benefits underscore the significance of SiO₂ encapsulation in achieving superior catalyst stability and activity.

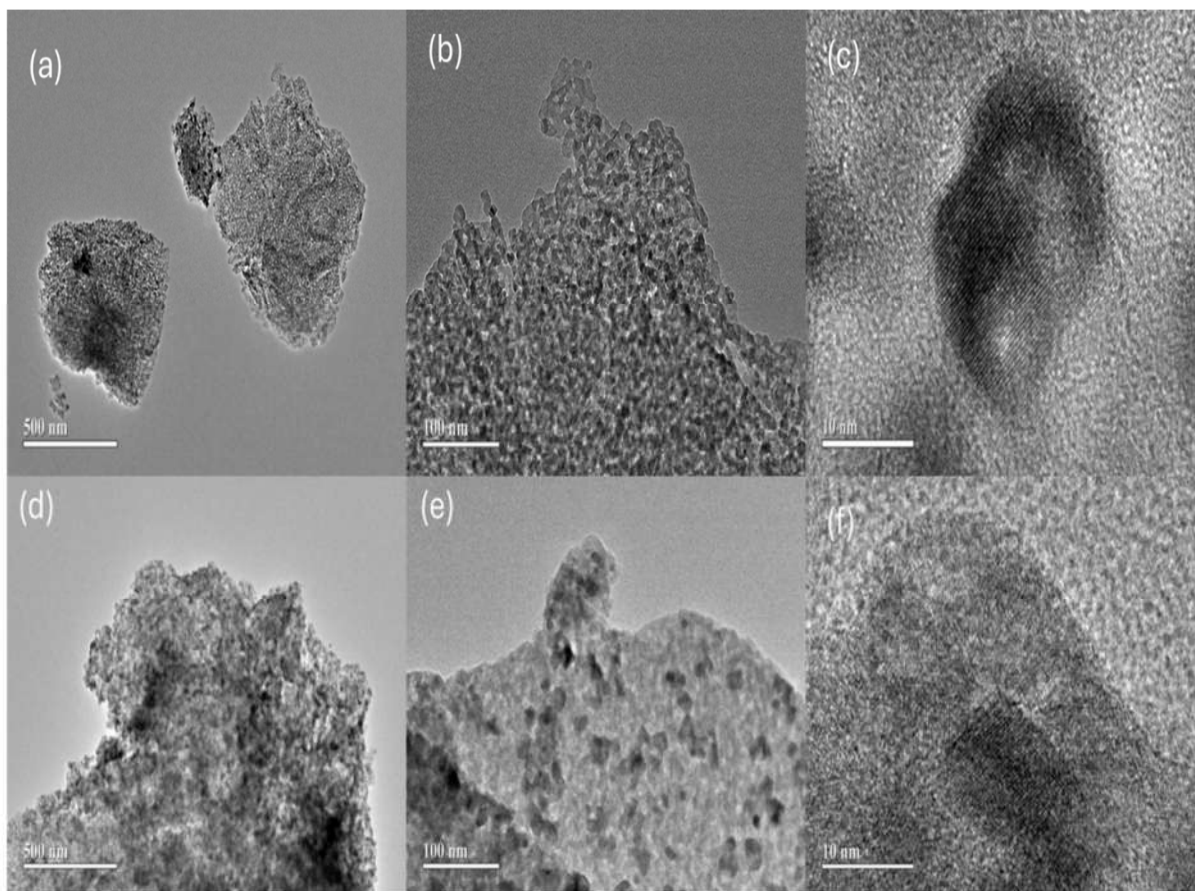


Figure 4.7: TEM images of the fresh catalysts; (a-c) Ni/Ce-Al₂O₃, (d-f) Ni/Ce-Al₂O₃@SiO₂

4.3 Catalyst performance and stability

Figure 4.8 shows the CH₄ conversion profiles at 650 °C over Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ catalysts at varying reaction times during DRM. At 5 and 10 seconds, both catalysts show increasing activity, with the encapsulated catalyst achieving higher conversions (38.5% and 45.5%) compared to the bare counterpart (34.6% and 42.9%). A peak conversion of 50.4% is observed for Ni/Ce-Al₂O₃@SiO₂ at 15 seconds, followed by a slight drop to 48.8% at 20 seconds, likely due to partial CO₂ hydrogenation within the confined SiO₂ shell. Ni/Ce-Al₂O₃ shows a steady rise, reaching 46.5% at 20 seconds. Overall, conversions plateau beyond 10 seconds, suggesting it may be an optimal residence

time under the tested conditions. The improved performance of the encapsulated catalyst confirms the positive role of SiO₂ in enhancing activity and stability.

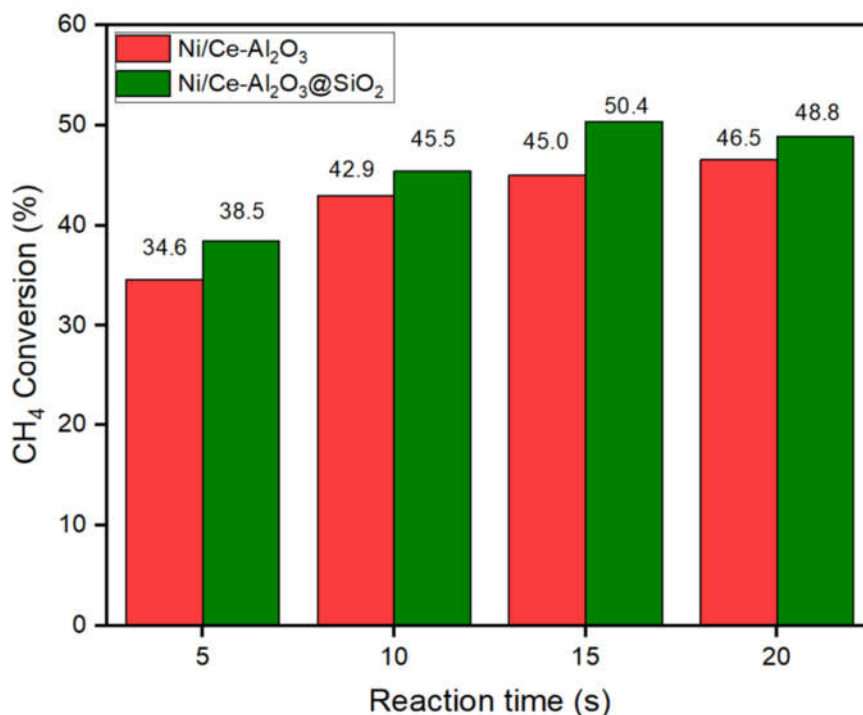


Figure 4.8: Methane conversion during DRM over bare Ni/Ce-Al₂O₃, and encapsulated Ni/Ce-Al₂O₃@SiO₂

Building on the CH₄ conversion, the CO₂ conversion (Figure 4.9) further highlight the enhanced performance of Ni/Ce-Al₂O₃@SiO₂ catalyst. At all residence times, Ni/Ce-Al₂O₃@SiO₂ consistently outperformed Ni/Ce-Al₂O₃, achieving a maximum of 73.8% CO₂ conversion at 20 seconds, compared to 58.7% for unencapsulated catalyst. The higher activity is attributed to improved Ni dispersion and surface basicity, which facilitate more efficient CO₂ adsorption and activation, as supported by CO-chemisorption and CO₂-TPD

data. While a slight fluctuation was observed between 10 and 15 seconds, the conversion stabilized thereafter, indicating a steady-state performance at longer times.

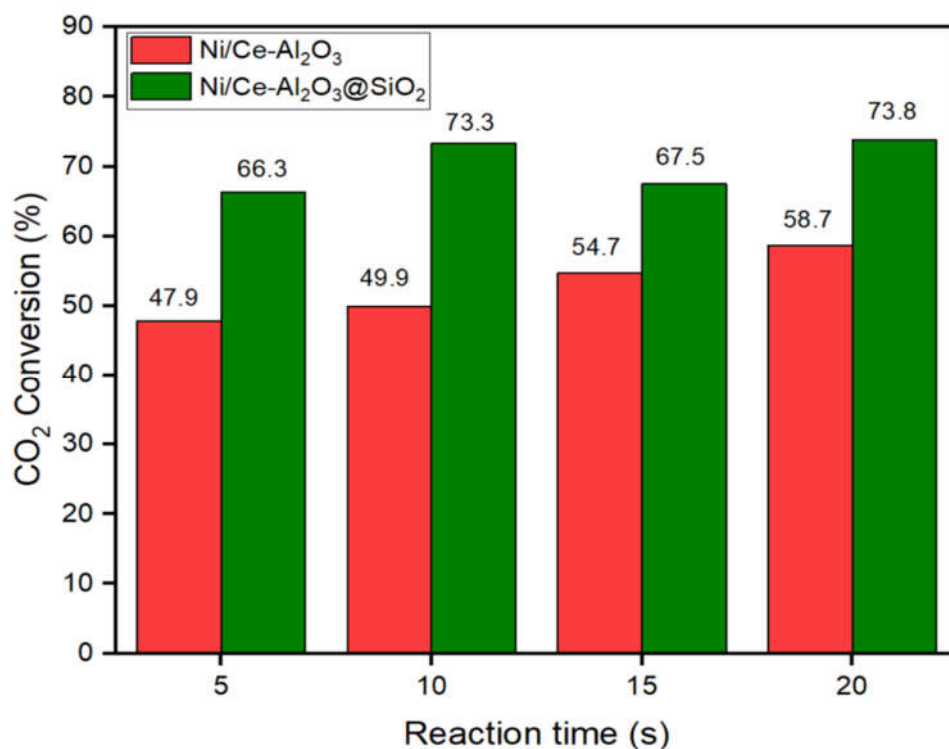


Figure 4.9: CO₂ conversion during DRM over bare Ni/Ce-Al₂O₃, and encapsulated Ni/Ce-Al₂O₃@SiO₂

The stability of the catalysts was evaluated over 10 consecutive DRM cycles by repeatedly injecting CH₄ and CO₂ without regeneration of the catalyst between runs. The Ni/Ce-Al₂O₃@SiO₂ catalyst exhibited consistently higher CH₄ and CO₂ conversions compared Ni/Ce-Al₂O₃ as shown in Figure 4.10a,b, highlighting the positive impact of silica encapsulation. Both catalysts demonstrated good stability, with fluctuations remaining within $\pm 5\%$ of their respective mean conversion values, indicating resistance to deactivation over time. The encapsulated catalyst's superior and stable performance can be

attributed to the protective silica shell, which mitigates sintering and coke formation directly on the active Nickel sites. The stability of the H_2/CO ratio over 10 cycles (Figure 4.10c) further underscores the robustness of both catalysts. The $Ni/Ce-Al_2O_3$ catalyst maintained a slightly higher H_2/CO ratio (~ 1.2), while the $Ni/Ce-Al_2O_3@SiO_2$ catalyst exhibited a stable ratio around 1.0–1.1. The consistent H_2/CO ratios across cycles indicate steady syngas selectivity and minimal fluctuations in the reaction pathways, reflecting both catalysts' resistance to deactivation. The slightly lower ratio observed for the encapsulated catalyst may be attributed to the moderated methane decomposition and improved CO_2 activation promoted by the silica shell, which balances hydrogen and CO production while suppressing carbon formation.

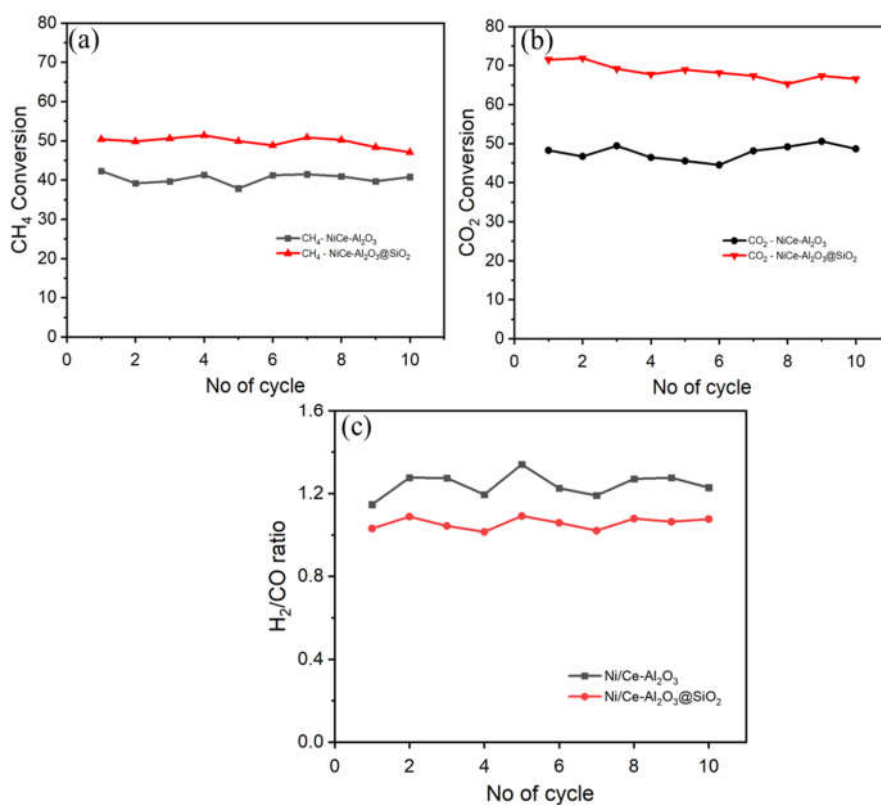


Figure 4.10: Stability test of $Ni/Ce-Al_2O_3$ & $Ni/Ce-Al_2O_3@SiO_2$ over 10 cycles (a) CH_4 Conversion (b) CO_2 Conversion (c) H_2/CO ratio

4.4 Spent catalyst characterization

X-ray diffraction (XRD) analysis of the spent Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ after reaction reveals that the primary crystalline phases; NiO, NiAl₂O₄ spinel, and γ -Al₂O₃ remain largely unchanged, indicating robust structural stability under reaction conditions as shown in **Error! Reference source not found..** Notably, a broad peak observed around $2\theta \approx 20^\circ$ in the fresh catalysts, attributed to NiO and γ -Al₂O₃ phases, was absent in the spent samples, suggesting possible structural reorganization or densification of the amorphous components during high-temperature exposure. Additionally, new diffraction peaks emerged at $2\theta \approx 39.6^\circ$ and 44.5° , with the latter appearing as a distinct shoulder from the main peak at 45.7° , corresponding to NiAl₂O₄ and γ -Al₂O₃. These new peaks indicate the formation of metallic Ni (Ni⁰) due to partial reduction under the reducing environment of DRM. The preservation of key crystalline phases and the emergence of the Ni⁰ underscore the catalysts stability over 10 reaction cycles without regeneration.

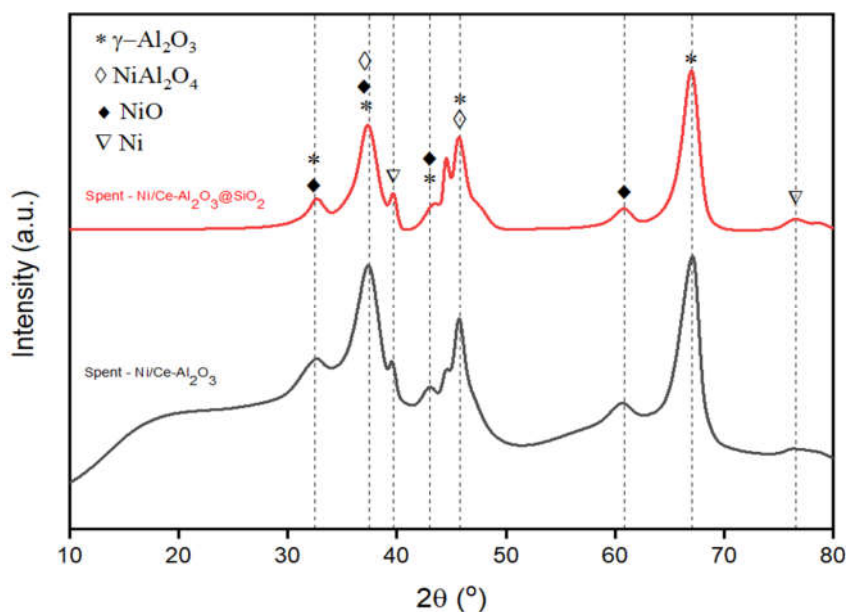


Figure 4.11: XRD spectra of the used catalyst

Figure 4.12 represents the thermograms of the used catalyst. The low temperature region (below 200 °C) reduction in catalyst weight ascribed to desorption of physical adsorbed water or volatile compounds on the catalyst. The weight reduction observed at intermediate temperatures (200-600 °C) is ascribed to the removal of the amorphous carbonaceous residues. on the catalyst and the high temperature region (above 600 °C) is attributed to the oxidation of high stability carbon such as graphitic carbon. The presence of this carbon has been earlier confirmed from the Raman spectrum. For the Ni/Ce-Al₂O₃, the thermograms profile show weight loss at intermediate and high temperature regions, indicating high coke formation during the DRM reaction. The higher weight loss indicates generation of carbon on the catalyst which can be associated with direct exposure of the Ni active site to the reaction gases leading to the deposition of carbon due to CH₄ cracking and CO disproportionation. It should be noted however, that the later reaction (i.e., Boudouard reaction, which is favorable at low temperature, below 500°C) may not be

dominant at the reaction temperature of 650 °C. In contrast, Ni/Ce-Al₂O₃@SiO₂ shows very minimal weight loss in both the intermediate and high temperature regions. This suggests significantly low coke formation due to the presence of mesoporous silica shell which acts as a barrier confining the Ni nanoparticles. The higher catalyst weight loss observed in the unencapsulated catalyst as compared to the encapsulated catalyst could be attributed to an easier removal of carbon deposit which facilitates gas diffusion and carbon oxidation.

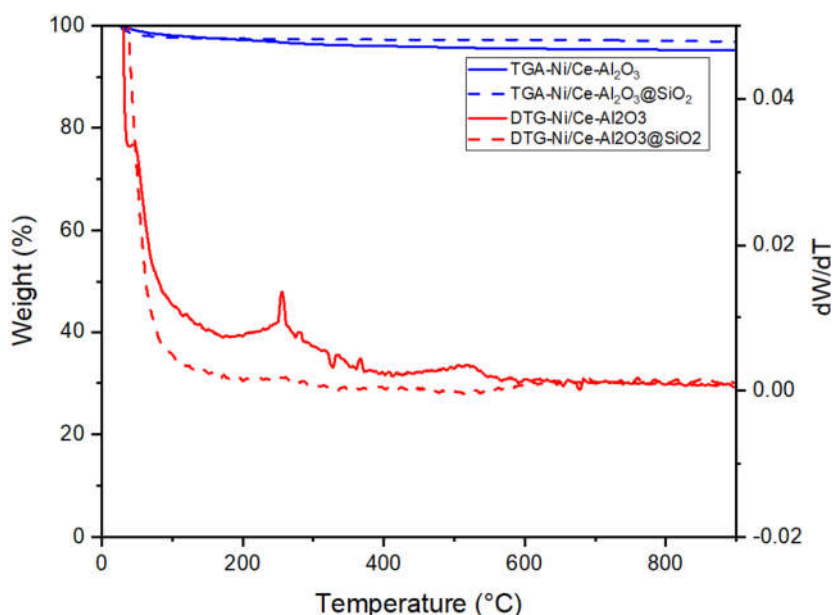


Figure 4.12: TGA and DTG of the used catalyst

The carbon resistance of the spent Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃@SiO₂ catalysts was further evaluated using Raman spectroscopy to support the thermogravimetric analysis (TGA). As shown in Figure 4.13, the Raman spectra of both catalysts exhibit broad, unresolved bands centered near ~2500 cm⁻¹, with no weak D (~1350 cm⁻¹) and G (~1580 cm⁻¹) bands typically associated with disordered or graphitic carbon [33], [35],

[34]. This absence of sharp characteristic carbon peaks implies minimal accumulation of structured carbon species and reflects either a highly disordered or low-concentration carbon presence. Notably, the encapsulated $\text{Ni/Ce-Al}_2\text{O}_3@\text{SiO}_2$ catalyst displayed an even weaker signal across this region, further reinforcing its resistance to carbon formation.

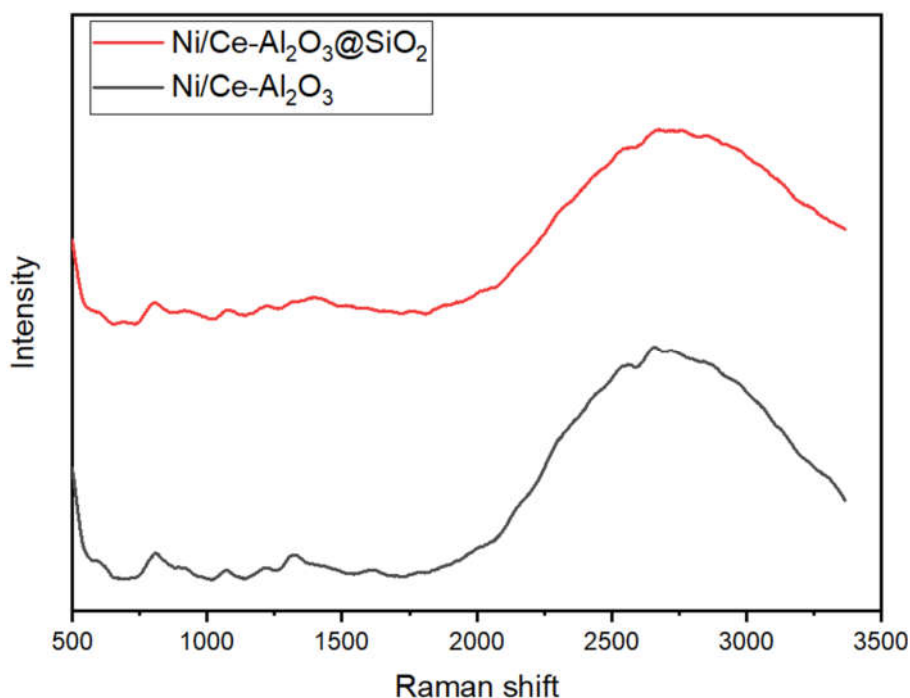


Figure 4.13: Raman Spectra of the used catalyst

After the reaction with CH_4 and CO_2 , significant changes were observed in the morphology of the spent catalyst. These transformations can be attributed to the formation of carbon deposits, which were clearly identified as tube-like structures in Figure 4.14 a,b. The EDS mapping (Figure 4.14 c,d) of the spent catalyst highlights the distribution of Ni, Ce, Al, and Si across the catalyst surface. Additionally, the EDS X-ray spectra (Figure 4.14 e,f) provide a quantitative analysis of the elements present within the selected regions, confirming the composition of the catalyst. The formation of carbon deposits observed in

the SEM images aligns with the findings from the Raman spectra, further validating the presence of carbon on the spent catalyst.

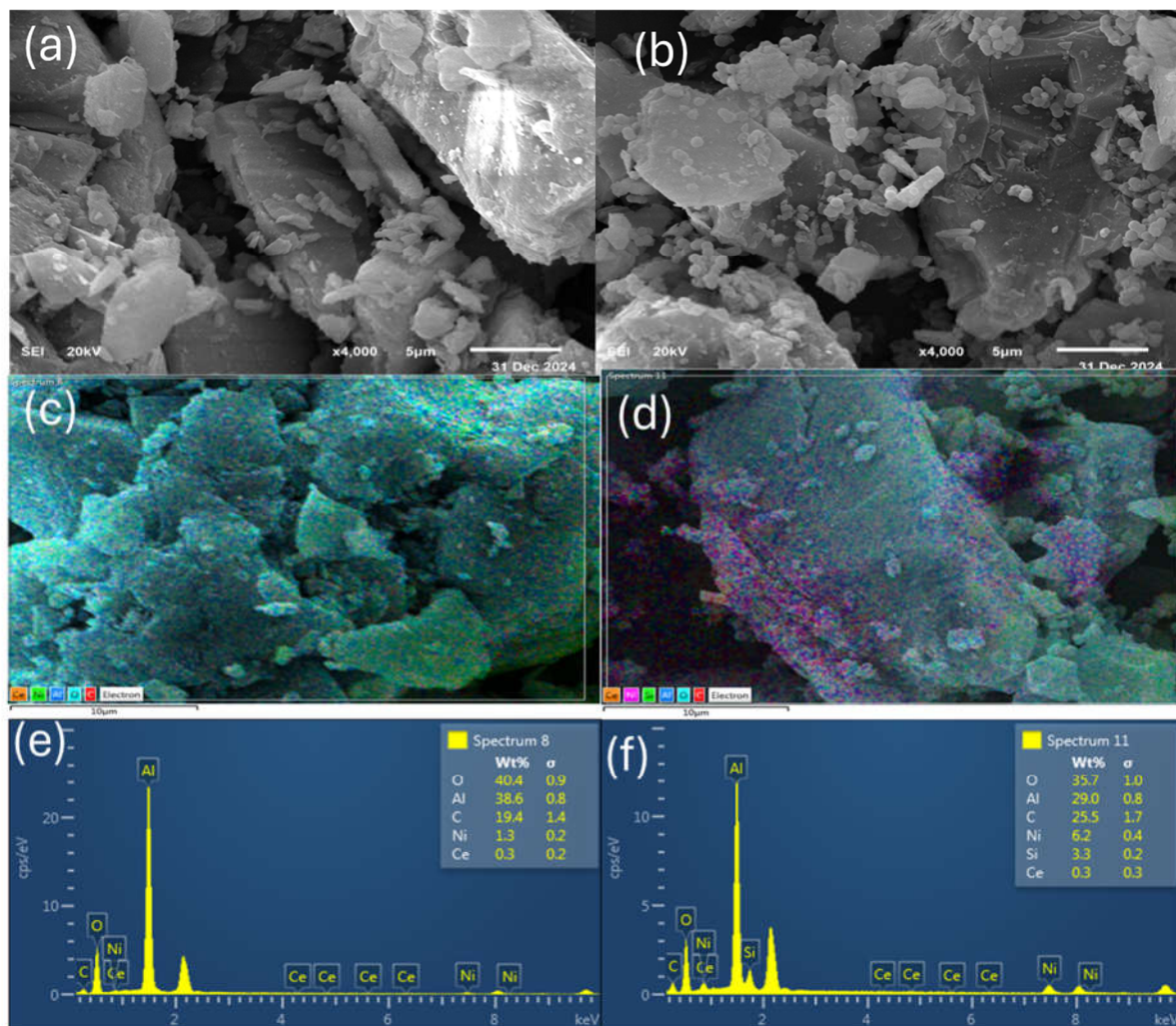


Figure 4.14: SEM images of spent catalyst (a) Ni/Ce-Al₂O₃ (b) Ni/Ce-Al₂O₃@SiO₂ (c) EDS-Mapping Ni/Ce-Al₂O₃ (d) EDS-Mapping Ni/Ce-Al₂O₃@SiO₂ (e) EDS X-ray spectra Ni/Ce-Al₂O₃ (f) EDS-Mapping Ni/Ce-Al₂O₃@SiO₂

The TEM images of the spent catalyst shown in Figure 4.15 (a–c) as representative of Ni/Ce-Al₂O₃, whereas Figure 4.15(d–f) illustrate Ni/Ce-Al₂O₃@SiO₂. A clear morphological difference is observable in both catalysts when aligned with their untouched

counterparts, hinting at their responsiveness to methane (CH_4) and carbon dioxide (CO_2) in the catalytic activity. At 500 nm magnification (Figure 4.15a and d), the distinct encapsulation morphology of SiO_2 within the $\text{Ni/Ce-Al}_2\text{O}_3@\text{SiO}_2$ catalyst is conspicuously evident, manifesting as spherical entities that envelop the nickel particles. Conversely, the non-encapsulated $\text{Ni/Ce-Al}_2\text{O}_3$ exhibits no analogous morphology, underscoring the protective function of SiO_2 encapsulation. At 200 nm magnification, remnants of carbonaceous deposits are discernible on both catalysts. For the non-encapsulated $\text{Ni/Ce-Al}_2\text{O}_3$ (Figure 4.15 b), the carbon manifests as a composite of amorphous carbon (irregular, featureless black regions) alongside some indications of carbon nanotubes (CNTs) in tubular configurations. In the encapsulated $\text{Ni/Ce-Al}_2\text{O}_3@\text{SiO}_2$ (Figure 4.15e), although analogous carbon structures are apparent, the encapsulation layer seems to alleviate excessive aggregation of carbon deposits on the catalyst surface. Across all magnifications, the presence of carbon deposits is consistently observed, corroborating the generation of carbon during the catalytic reaction. The information we gathered corresponds effectively with the results from Raman spectroscopy and Scanning Electron Microscopy (SEM), which further validated the qualities and scale of carbon deposition. The SiO_2 encapsulation appears to assume a pivotal role in preserving catalyst integrity by constraining excessive carbon formation and agglomeration.

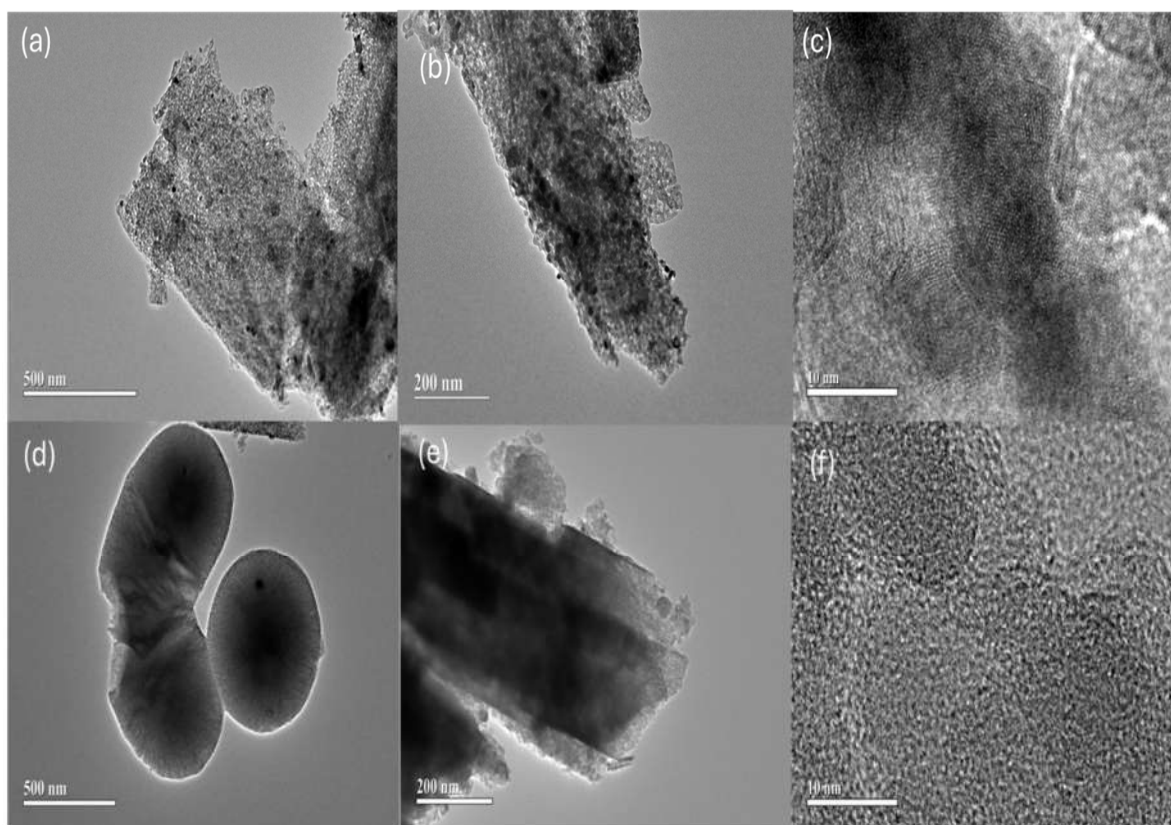


Figure 4.15: TEM images of the spent catalysts; (a-c) Ni/Ce-Al₂O₃, (d-f) Ni/Ce-Al₂O₃@SiO₂

This chapter presented an in-depth characterization and catalytic activity of Ni/Ce-Al₂O₃ and Ni/Ce-Al₂O₃ for DRM. XRD analyses confirmed the presence of key crystalline phases such as NiO, NiAl₂O₄, and γ -Al₂O₃, with silica encapsulation preserving crystallinity while enhancing thermal stability. TPR and TPD studies revealed that encapsulation moderately shifted Ni reduction to higher temperatures and increased surface basicity, favoring CO₂ activation. BET analysis indicated a significant increase in surface area and porosity upon SiO₂ coating, while CO chemisorption confirmed improved metal dispersion and surface accessibility. Morphological investigations using SEM and TEM further highlighted the role of SiO₂ in maintaining nanoscale Ni distribution and preventing particle sintering.

Performance tests at 650 °C showed that Ni/Ce–Al₂O₃@SiO₂ consistently outperformed the unencapsulated catalyst, achieving higher CH₄ and CO₂ conversions and maintaining over 95% activity after 10 DRM cycles without regeneration. Overall, the study demonstrated that SiO₂ encapsulation significantly enhances catalyst activity, structural integrity, and resistance to deactivation in DRM conditions.

CHAPTER 5

Catalyst Evaluation – Ni/CaO-Al₂O₃ & Ni/CaO-Al₂O₃@SiO₂

5.1 Introduction

Ni-based catalysts promoted with CaO have gained attention for DRM due to their enhanced basicity, which improves CO₂ adsorption and reduces carbon formation. The addition of CaO into Al₂O₃ can significantly improve metal dispersion and thermal resistance due to the formation of mixed phases like CaAl₂O₄. However, challenges such as Ni sintering and coke formation still limit long-term stability. To address this, silica encapsulation of the catalyst was adopted, Ni/CaO-Al₂O₃@SiO₂, was developed to confine Ni particles and have SiO₂ as the shell surrounding the Ni/CaO-Al₂O₃ catalyst. This chapter evaluates the structural and catalytic performance of both Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂. Characterization techniques and DRM testing were used to assess the effects of silica encapsulation on catalyst activity, stability, and coke resistance.

5.2 Catalyst characterization and morphology

The XRD pattern of Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ is shown in Figure 5.1: XRD Pattern of calcined Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂. Both catalysts exhibited sharp peaks at $2\theta \approx 37.2^\circ$, 43.3° , and 62.9° , which are attributed to metallic Ni, while signals around $29\text{--}34^\circ$ correspond to CaO and CaAl₂O₄ phases [102]. These reflections confirm the crystalline nature of the catalyst and the presence of well-defined Ni particles. Notable for Ni/CaO-Al₂O₃@SiO₂ showed a significant drop in Ni peak intensity, along

with broader peaks. This suggests a reduction in Ni crystallite size and improved dispersion, likely due to the confinement effect of the SiO₂ shell. Overall, the decrease in Ni crystallinity suggests the formation of smaller, more uniformly dispersed Ni particles, likely stabilized by the silica shell. Such structural features are beneficial for DRM, as they limit sintering and reduce carbon accumulation, thereby enhancing both catalyst stability and long-term performance.

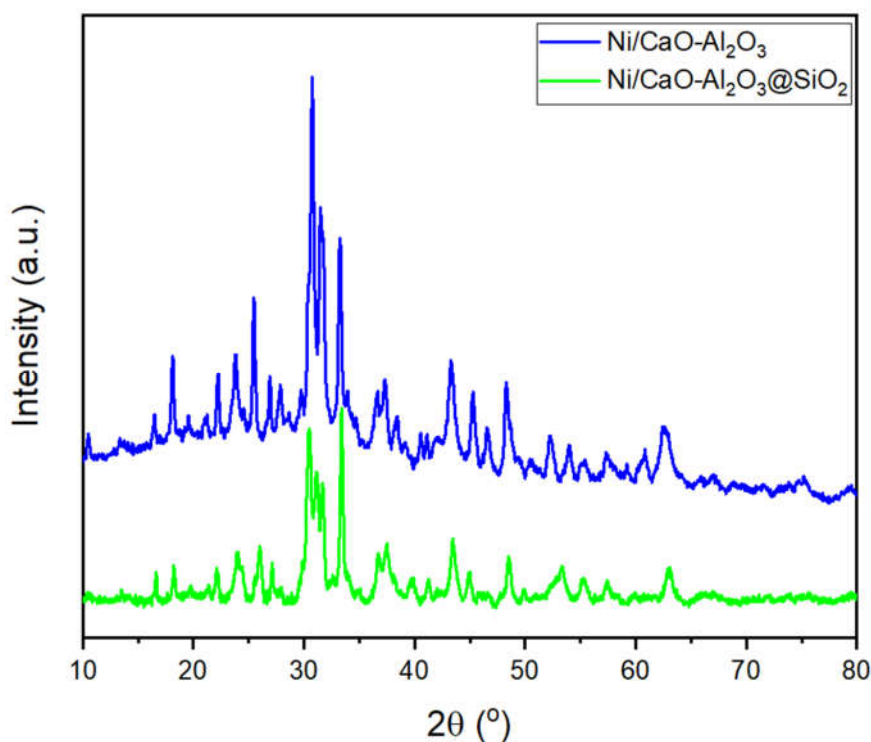


Figure 5.1: XRD Pattern of calcined Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂

The H₂-TPR profiles of both catalysts shown in Figure 5.2 revealed distinct differences in their reducibility. For Ni/CaO-Al₂O₃, a prominent reduction peak was observed at low temperature within 350–550 °C, suggesting the presence of NiO species that are weakly bonded to the support. This indicates a relatively easier reduction process but also implies

a risk of Ni particle agglomeration at high temperatures due to weaker metal-support interactions. On the other hand, the encapsulated Ni/CaO-Al₂O₃@SiO₂ catalyst exhibited a broader peak shifted toward higher temperatures, ranging approximately from 500 to 700 °C. This shift is a typical indication of stronger interactions between Ni species and the support, likely due to the confinement effect of the silica shell. The broader distribution may also point to a mix of Ni species some more accessible and others more embedded which could contribute to improved thermal stability during reforming. In essence, the silica shell enhances metal-support interaction, making Ni species more thermally stable and less prone to sintering.

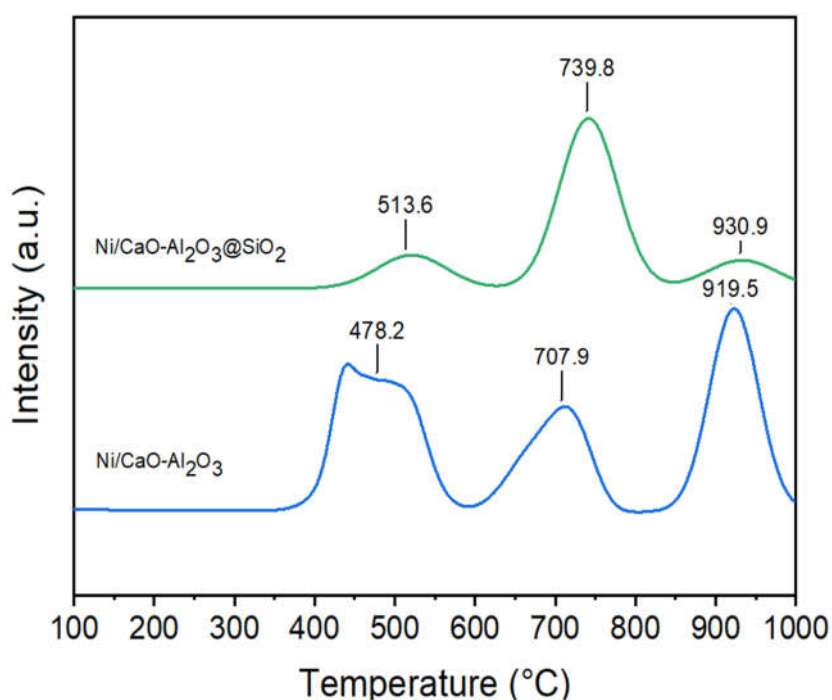


Figure 5.2: H₂ – TPR Profile of calcined Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂

The NH₃-TPD profiles (Figure 5.3) revealed distinct acidity patterns between the two catalysts. Ni/CaO-Al₂O₃ showed a major desorption peak around 200 °C, indicating the

presence of weak acid sites, likely from the alumina surface. In contrast, Ni/CaO-Al₂O₃@SiO₂ exhibited a broader and more intense peak between 250–300 °C, with tailing beyond 400 °C. This suggests an increase in both the density and strength of acid sites, attributed to the effect of the silica shell. The enhanced surface acidity may facilitate better CO₂ adsorption and contribute to improved resistance to carbon deposition during DRM.

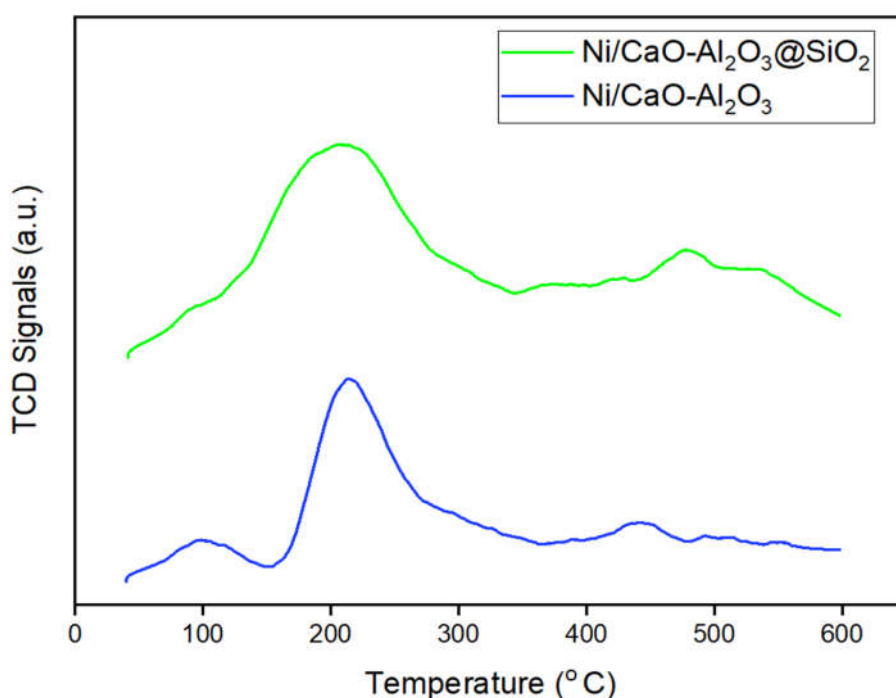


Figure 5.3: NH₃ – TPD of Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂

The nitrogen adsorption–desorption isotherms (Figure 5.4a,b) of Ni/CaO–Al₂O₃ and Ni/CaO–Al₂O₃@SiO₂ demonstrate distinct differences in their textural properties. Both catalysts display type IV isotherms with H₃-type hysteresis loops, typical of mesoporous structures. However, Ni/CaO–Al₂O₃@SiO₂ catalyst exhibits a more pronounced uptake at high relative pressures, indicating the formation of larger mesopores. This is consistent with the data in Table 5.1, where a substantial increase in surface area from 19.6 to

54.8 m²/g and a significant shift in average pore diameter from 13.74 to 54 nm are observed. While the total pore volume slightly decreased upon encapsulation (from 0.13 to 0.11 cm³/g), the broader pore distribution introduced by the silica shell is expected facilitate improved gas diffusion and reduce mass transfer limitations during DRM.

Table 5.1: Textural Properties of Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ Catalysts

Catalyst	Surface Area (m ² /g)	Total Pore Volume (cm ³ g ⁻¹)	Ads. Avg. pore diameter (nm)
Ni/CaO-Al ₂ O ₃	19.6	0.13	13.74
Ni/CaO-Al ₂ O ₃ @SiO ₂	54.8	0.11	54

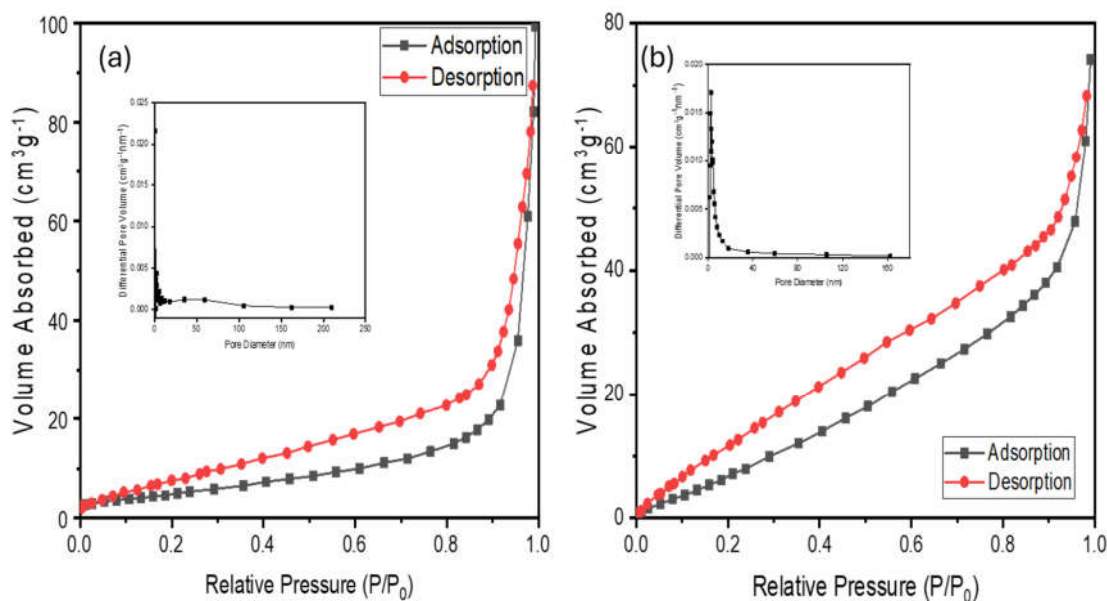


Figure 5.4: BET Analysis of the fresh catalyst (a) Ni/CaO-Al₂O₃ (b) Ni/CaO-Al₂O₃@SiO₂

These textural enhancements correlate well with the CO-chemisorption results presented in Table 5.2. The encapsulated catalyst exhibited a higher metal dispersion (2.87%) and greater metallic surface area (0.96 m²/g sample) compared to Ni/CaO-Al₂O₃ (2.54% and

0.85 m²/g, respectively). Moreover, the particle diameter decreased from 39.74 nm to 35.26 nm after encapsulation, suggesting that the silica shell effectively inhibits Ni particle agglomeration and preserves active surface area. Collectively, the BET and chemisorption results underscore the critical role of SiO₂ encapsulation in tailoring the structural and surface properties of the catalyst, ultimately leading to improved activity and stability under harsh reaction conditions.

Table 5.2: Surface and Structural Properties of Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ via CO Chemisorption

Catalyst	Metal Dispersion (%)	Metal Surface Area (m ² /g sample)	Metal Surface Area (m ² /g metal)	Particle diameter (nm)
Ni/CaO-Al ₂ O ₃	2.54	0.85	16.96	39.74
Ni/CaO-Al ₂ O ₃ @SiO ₂	2.87	0.96	19.12	35.26

TEM images of the calcined Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ catalysts are presented in Figure 5.5. Ni/CaO-Al₂O₃ (Figure 5.5, a–b) exhibited irregularly shaped particles with dispersed, loosely aggregated nickel species, indicating relatively weaker particle-support interactions. Such morphology might lead to particle agglomeration under DRM conditions. Conversely, the Ni/CaO-Al₂O₃@SiO₂ catalyst (Figure 5.5, c–d) clearly showed spherical core-shell structures with uniform particle distribution, confirming effective silica encapsulation. The silica layer appears thin and continuous, providing structural confinement, which could significantly minimize Ni particle migration, reduce sintering, and enhance catalyst stability during reaction.

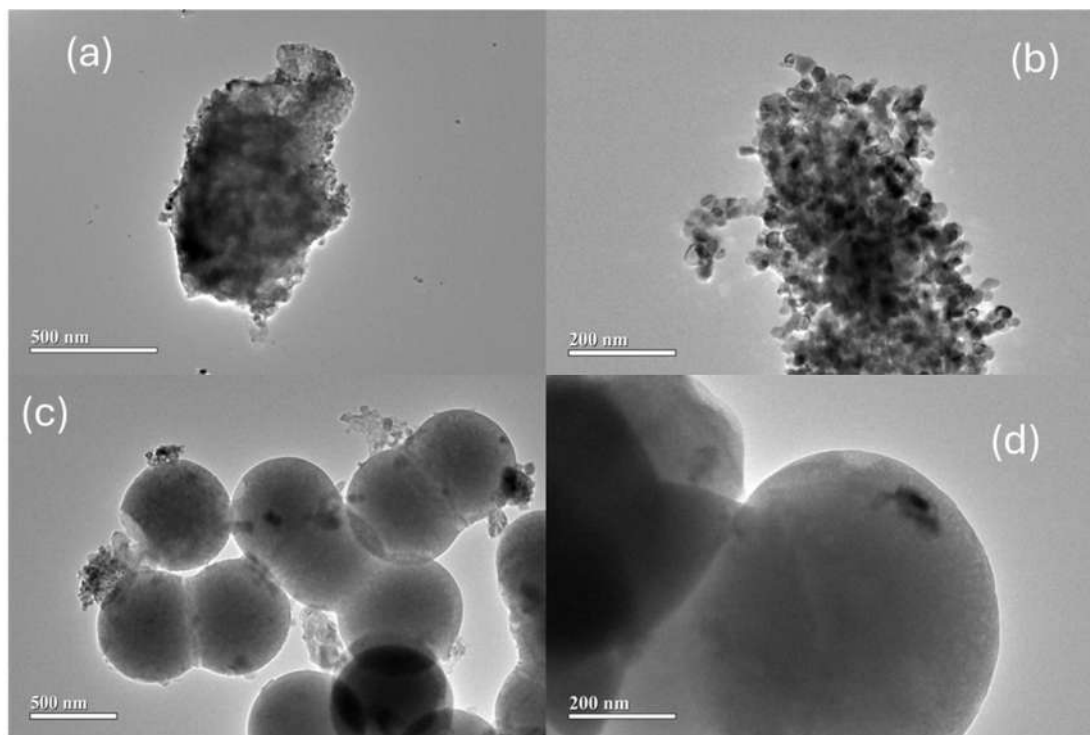


Figure 5.5: TEM images of fresh catalyst (a-b) Ni/CaO-Al₂O₃ (c-d) Ni/CaO-Al₂O₃@SiO₂

5.3 Catalyst activity evaluation

The catalytic performance for methane (CH₄) and carbon dioxide (CO₂) conversions over Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ are shown in Figure 5.6. Both catalysts exhibited high initial conversions, which indicates strong catalytic activity for DRM. The silica-encapsulated catalyst, Ni/CaO-Al₂O₃@SiO₂, consistently showed superior CH₄ and CO₂ conversions compared to its non-encapsulated counterpart. This improvement aligns with earlier characterization findings, particularly better Ni dispersion and higher surface acidity due to SiO₂ encapsulation, thus facilitating enhanced gas–solid interactions and more efficient reactant conversion. However, slight decreases observed in conversions at extended reaction times (around 15–20 s) suggest potential side reactions occurring. These side reactions, likely including Reverse Water Gas Shift (RWGS) and carbon-forming

reactions such as methane decomposition, could partially block active sites, leading to reduced conversions. The encapsulated catalyst's smaller decline in activity indicates improved resistance to such deactivation pathways. Thus, encapsulation not only enhanced overall catalytic efficiency but also provided better resilience against catalyst deactivation mechanisms typical in DRM processes.

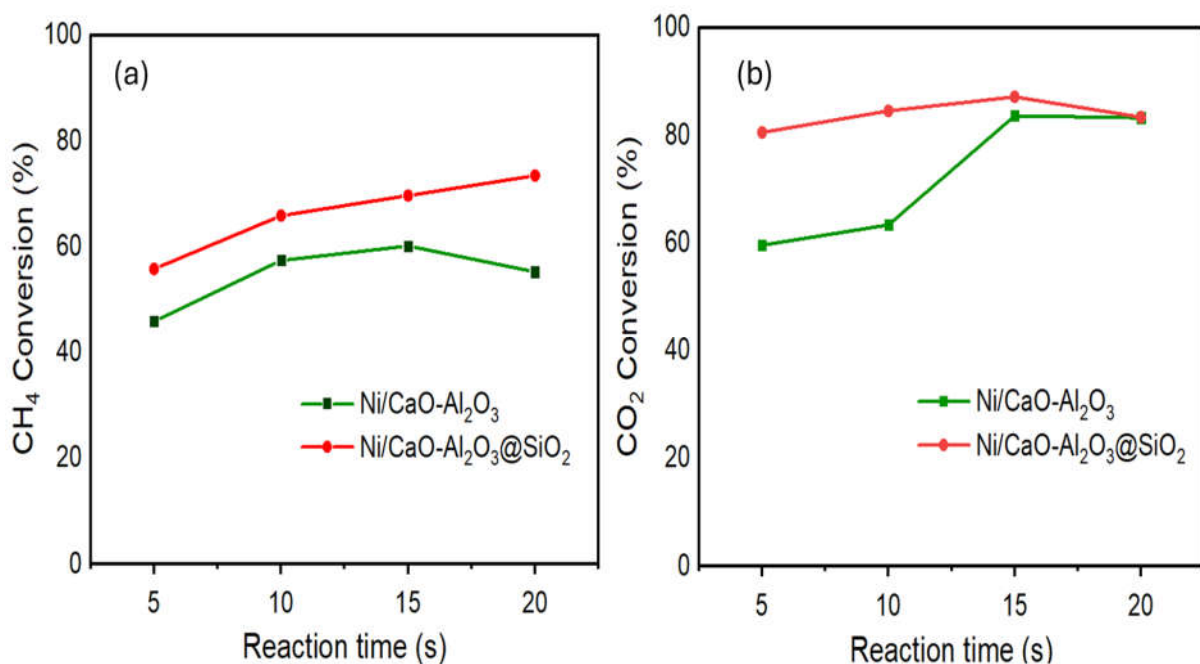


Figure 5.6: Catalytic performance for DRM (a)CH₄ conversion (b) CO₂ conversion

The yields of hydrogen (H₂) and carbon monoxide (CO) for both Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ catalysts are presented in Figure 5.7. For H₂ yield, Ni/CaO-Al₂O₃ started around 34% at 5 s and steadily increased to approximately 63% at 15 s, beyond which the yield plateaued. In comparison, Ni/CaO-Al₂O₃@SiO₂ exhibited a higher initial H₂ yield (~54% at 5 s), consistently increasing to approximately 68% at 20 s, highlighting improved catalytic activity and stability. Similarly, CO yield showed a similar trend. The Ni/CaO-Al₂O₃ catalyst provided an initial CO yield of approximately 60%, which

increased to around 75% at 15 s, and then slightly decreased at extended reaction times. Meanwhile, the encapsulated Ni/CaO-Al₂O₃@SiO₂ maintained consistently higher yields, starting around 72% and gradually reaching approximately 80% at 20 s. The enhanced yields with silica encapsulation likely result from improved Ni dispersion, higher catalyst acidity, and stronger resistance against carbon deposition and particle sintering, as previously confirmed by characterization results.

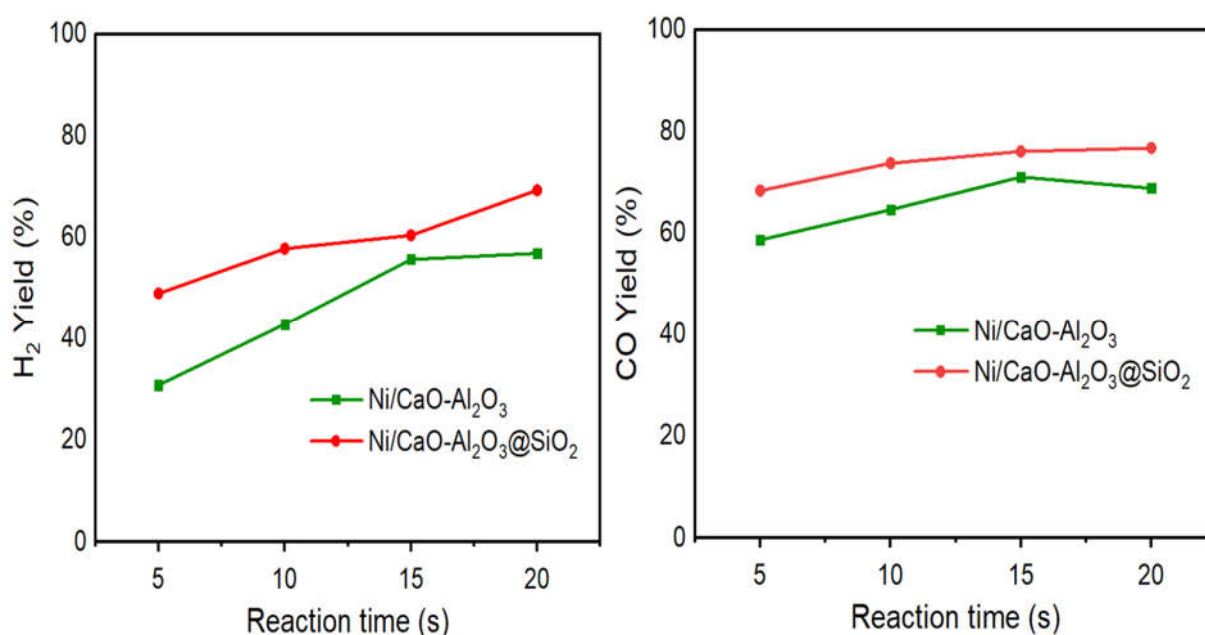


Figure 5.7: Catalytic performance for DRM (a)H₂ yield (b) CO yield

The stability of Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ was assessed over 10 consecutive reaction cycles without regeneration (Figure 5.8). Both CH₄ and CO₂ conversions were tracked to evaluate deactivation trends. For Ni/CaO-Al₂O₃, CH₄ conversion dropped from ~52% to ~48% over the 10 cycles, while CO₂ conversion declined from ~60% to ~56%. This reduction suggests gradual deactivation, possibly due to coke accumulation or Ni sintering, consistent with the limited structural stability observed in characterization. In

contrast, Ni/CaO-Al₂O₃@SiO₂ showed significantly better retention of activity. CH₄ conversion remained steady around 63–65%, while CO₂ conversions maintain values around 75% throughout the 10 cycles. The improved durability is likely attributed to the SiO₂ shell, which stabilizes Ni particles and reduces surface carbon buildup, thereby minimizing active site loss. These results affirm that silica encapsulation plays a vital role in enhancing catalyst longevity under DRM conditions.

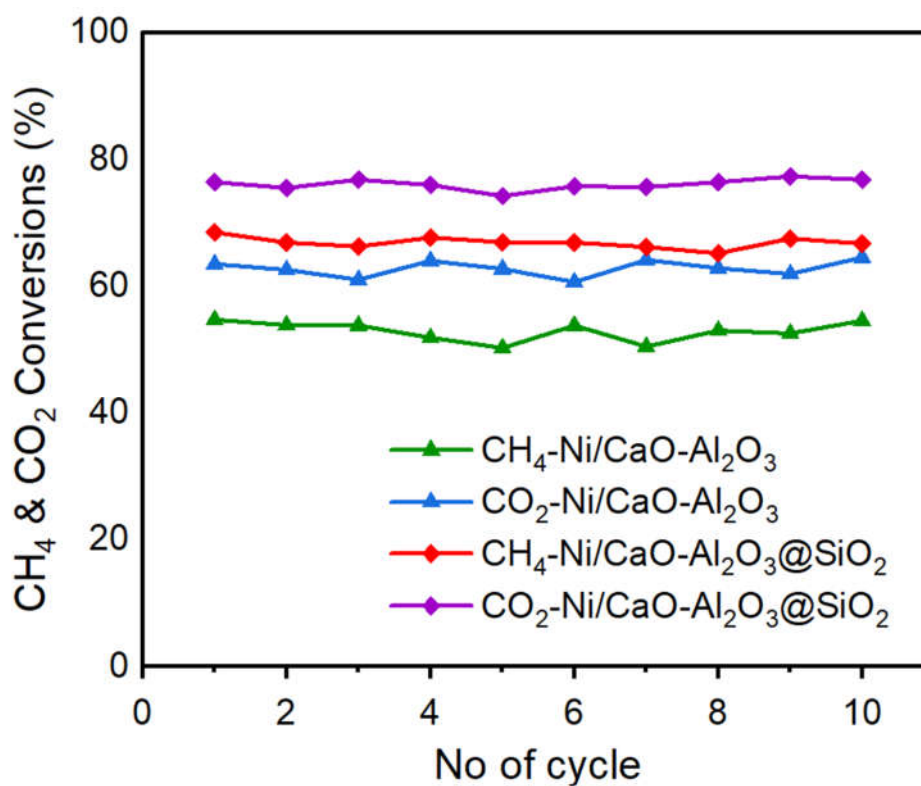


Figure 5.8: Catalyst stability: CH₄ and CO₂ conversions

5.4 Spent catalyst characterization

TGA results of the spent catalysts (Figure 5.9) showed negligible weight loss across the full temperature range, with both catalysts retaining close to 100% of their initial weight. This indicates that the overall coke deposition during the DRM reaction was minimal,

likely due to effective reaction conditions and catalyst properties. However, the DTG profiles revealed key differences in the nature and amount of deposited carbon. The Ni/CaO-Al₂O₃ catalyst exhibited a broad oxidation peak near 630 °C, characteristic of amorphous carbon. This confirms that some level of coke was formed and could lead to deactivation over time. In contrast, Ni/CaO-Al₂O₃@SiO₂ showed only minor DTG peaks near 600 °C and 750 °C, indicating a much smaller amount of both amorphous and graphitic carbon. The silica shell likely prevented excessive CH₄ cracking and limited coke buildup by shielding the active Ni sites. These findings confirm the enhanced coke resistance of the encapsulated catalyst, aligning well with its superior performance and stability over multiple DRM cycles. In contrast, Ni/CaO-Al₂O₃@SiO₂ displayed a nearly flat DTG profile, indicating significantly lower carbon content. The silica shell likely acts as a barrier, limiting direct CH₄ decomposition on exposed Ni sites and suppressing carbon growth. These results validate the superior anti-coking behavior of the silica-encapsulated catalyst, consistent with its stable performance over repeated DRM cycles.

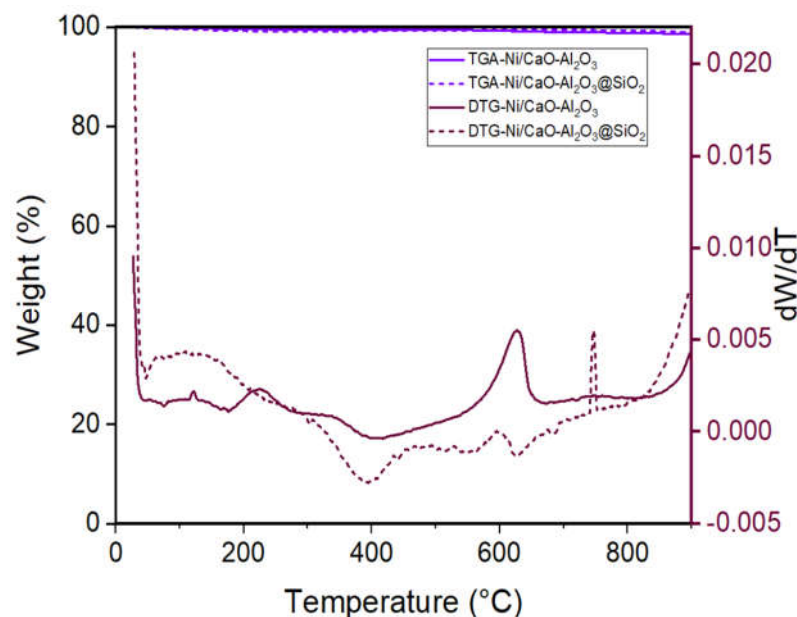


Figure 5.9: TGA and DTG of spent catalyst

XRD patterns of the spent catalysts (Figure 5.10) provide insight into structural changes following DRM. The spent Ni/CaO-Al₂O₃ catalyst shows a noticeable increase in the intensity and sharpness of Ni peaks ($2\theta \approx 43^\circ, 62.9^\circ$), compared to its fresh form. This suggests Ni particle growth due to sintering, which may contribute to the observed decline in catalytic activity over repeated cycles. The emergence of sharper peaks also indicates reduced metal dispersion post-reaction. In contrast, the spent Ni/CaO-Al₂O₃@SiO₂ retained a relatively similar diffraction pattern to its fresh state. The Ni peaks remained broad and less intense, implying that silica encapsulation effectively suppressed Ni sintering. No new phases were detected, and the support structure remained intact, confirming the enhanced structural stability of the encapsulated system. These results reinforce earlier findings from performance and TGA data, highlighting the role of the silica shell in maintaining catalyst integrity under harsh DRM conditions.

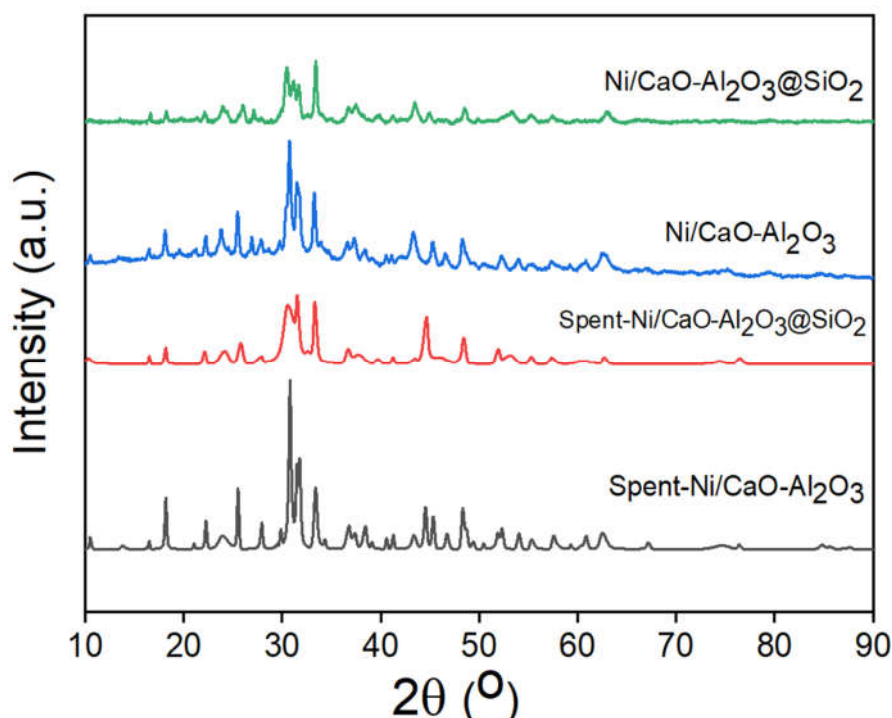


Figure 5.10: XRD patterns of spent catalyst

SEM micrographs reveal clear morphological differences between the spent catalysts. The Ni/CaO-Al₂O₃ catalyst (Figure 5.11a) displays rough, agglomerated particles with irregular surface features, suggesting potential sintering of Ni particles after repeated DRM cycles. Elemental mapping (Figure 5.11c) shows uneven Ni distribution, and the EDX spectrum (Figure 5.11e) confirms the presence of carbon, indicative of coke accumulation on the surface. This correlates with the DTG data and supports the observed drop in catalytic performance. In contrast, the Ni/CaO-Al₂O₃@SiO₂ (Figure 5.11b) retains a more uniform and spherical morphology. The particles appear to be well structurally dispersed, with fewer signs of structural collapse. Elemental mapping (Figure 5.11d) shows more homogeneous distribution of key elements, including Si, and the EDX result (Figure 5.11f) shows no carbon signal and alongside shows lower Ni signal intensity which may reflect

encapsulation within the silica shell, further explaining its improved resistance to sintering and coke formation.

Figure 5.12 shows the TEM images of the spent catalyst. This was carried out in order to investigate the coke formation after the stability test. These provides a clear insight into

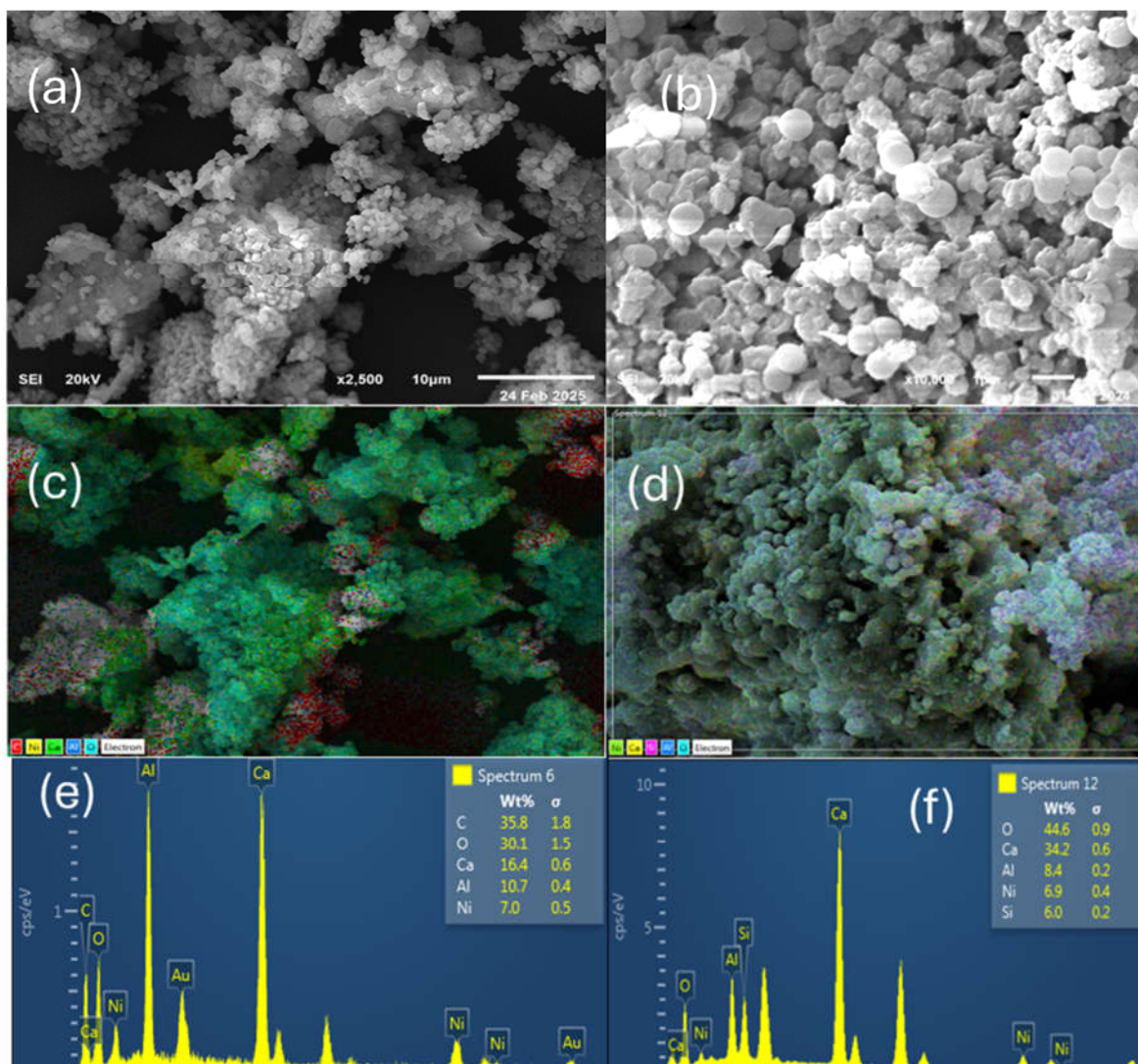


Figure 5.11: SEM images of spent catalyst (a) Ni/CaO-Al₂O₃ (b) Ni/CaO-Al₂O₃@SiO₂ (c) EDS-Mapping Ni/CaO-Al₂O₃ (d) EDS-Mapping Ni/CaO-Al₂O₃@SiO₂ (e) EDS X-ray spectra Ni/CaO-Al₂O₃ (f) EDS X-ray spectra Ni/CaO-Al₂O₃@SiO₂

the structural differences between the Ni/CaO-Al₂O₃ and Ni/CaO-Al₂O₃@SiO₂ catalysts.

For the Ni/CaO-Al₂O₃ catalyst (Figure 5.12, a-b), irregular aggregates with poorly defined

edges were observed, indicating uneven dispersion of Ni particles and potential susceptibility to particle agglomeration during DRM. In contrast, Ni/CaO-Al₂O₃@SiO₂ (Figure 5.12, c–d) displayed uniform spherical morphology with well-defined boundaries, confirming successful encapsulation by the silica shell. This uniform core–shell structure likely restricts Ni particle movement, enhancing dispersion and potentially improving thermal stability under reaction conditions. Overall, silica encapsulation notably improved structural uniformity and particle distribution, aligning well with earlier XRD and TPR findings.

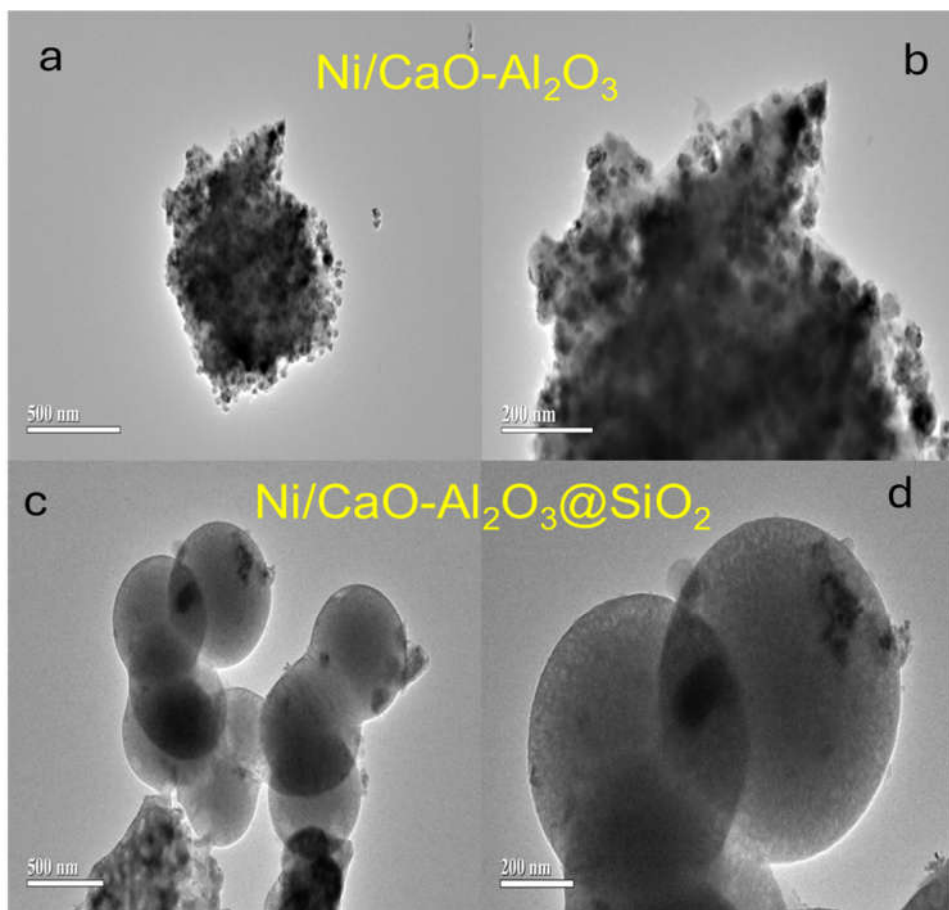


Figure 5.12: TEM images of spent catalyst (a-b) Ni/CaO-Al₂O₃ (c-d) Ni/CaO-Al₂O₃@SiO₂

This chapter focused on the in-depth evaluation of effect of SiO_2 encapsulation on $\text{Ni/CaO-Al}_2\text{O}_3$. Characterization results of the calcined samples confirmed improved metal-dispersion, stronger metal support interaction and enhanced surface acidity after encapsulation of $\text{Ni/CaO-Al}_2\text{O}_3$ with SiO_2 . The encapsulated catalyst showed higher CH_4 and CO_2 conversions, better H_2 and CO yields, and excellent stability over multiple cycles. Spent catalyst characterization analyses revealed significantly lower coke deposition, highlighting the effectiveness of silica encapsulation in improving catalyst durability under harsh DRM conditions.

CHAPTER 6

Catalyst Evaluation – Ni/Ce-Zr & Ni/Ce-Zr@SiO₂

6.1 Introduction

Following detailed evaluation of the Ni/Ce-Al₂O₃ and Ni/CaO-Al₂O₃ catalyst and their encapsulated pairs in the previous chapter, this section focuses on the Ni/Ce-Zr and Ni/Ce-Zr@SiO₂ for DRM. Ce-Zr mixed oxides are known for their strong redox properties and high oxygen mobility, which contribute to improved metal dispersion and reduced carbon accumulation during DRM. The following sections presents detailed evaluation of both catalysts to ascertain the effect of SiO₂ encapsulation on the Ni/Ce-Zr@SiO₂ catalyst.

6.2 Catalyst characterization and morphology

The XRD patterns of Ni/Ce-Zr and Ni/Ce-Zr@SiO₂ catalysts are shown in Figure 6.1: XRD pattern of calcined Ni/Ce-Zr and Ni/Ce-Zr@SiO₂. Both samples exhibit characteristic reflections at $2\theta \approx 29.1^\circ$, 33.6° , 37.4° , 43.4° , and 48.0° , which are attributed to the fluorite cubic structure of the CeO₂-ZrO₂ solid solution [103], [104]. This confirms successful integration of Ce and Zr oxides into a stable mixed oxide matrix. Additionally, the presence of peaks at 37.4° , 43.4° , and 77.15° in both catalysts suggests the formation of NiO, corresponding to the (111), (200), and (311) planes [86], [105]. These peaks are similar in both catalysts, indicating that the silica encapsulation did not significantly affect the crystallinity or detectable dispersion of NiO at this stage. No diffraction peaks related

to crystalline SiO_2 were observed, which is consistent with its expected amorphous nature. This is consistent with findings from chapter 4 and 5.

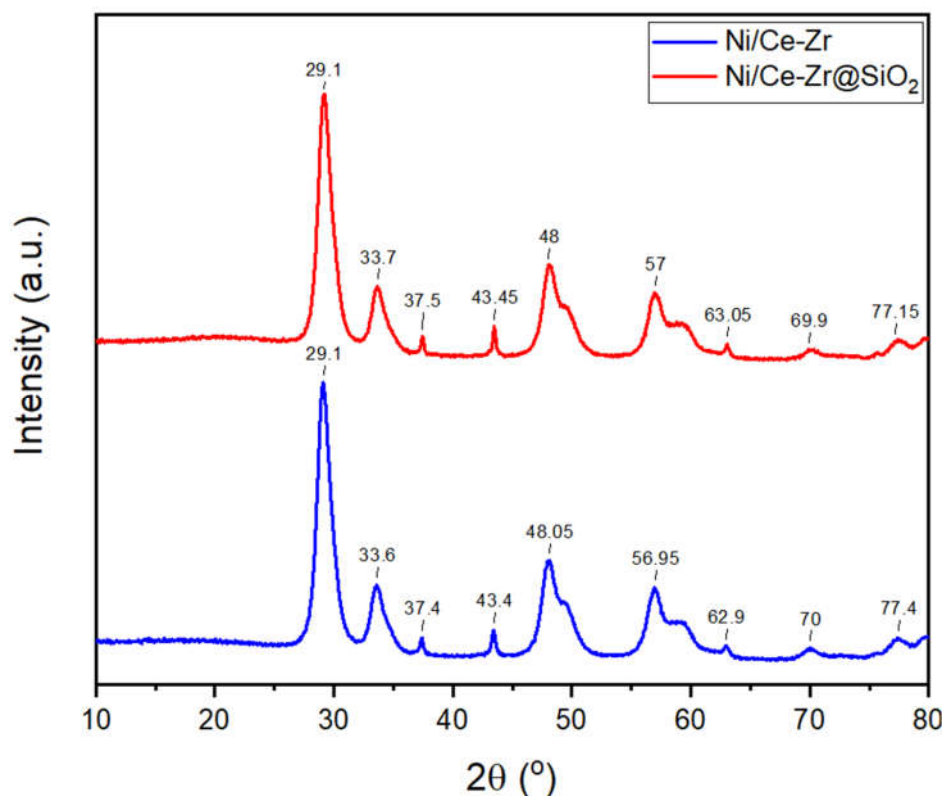


Figure 6.1: XRD pattern of calcined Ni/Ce-Zr and Ni/Ce-Zr@SiO₂

The reducibility of the calcined Ni/Ce-Zr and Ni/Ce-Zr@SiO₂ are presented in Figure 6. 2 Both catalysts exhibit multi-step reduction patterns, indicating the presence of Ni species with different reducibility strength with the Ce-Zr support. For Ni/Ce-Zr, several overlapping reduction peaks are observed between 300–500 °C, attributed to the stepwise reduction of NiO species. The initial peaks below 400 °C suggest the presence of weakly bound NiO, while the main peak around 430–450 °C corresponds to NiO species moderately interacting with the Ce-Zr support [106], [107]. In comparison, the Ni/Ce-Zr@SiO₂ catalyst shows a broader reduction peak, centered around 390–500 °C, indicating

reduced accessibility of NiO due to encapsulation. The extended peak at around 700 °C further supports the presence of more stabilized Ni species, likely embedded within the SiO₂ layer or interacting with the Ce–Zr framework. Overall, the encapsulated catalyst exhibits delayed and broader hydrogen consumption, suggesting improved thermal stability and resistance to Ni sintering under DRM conditions.

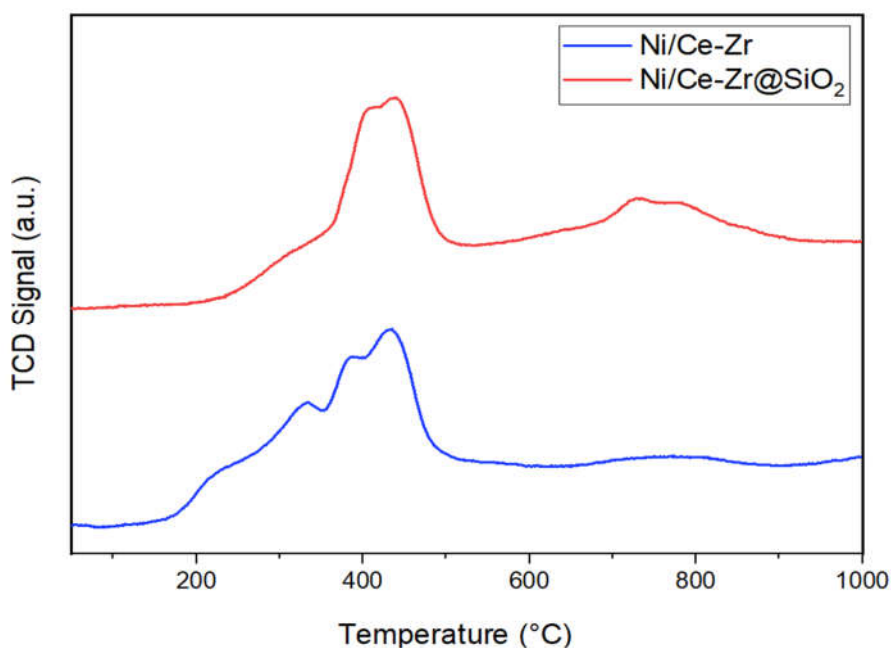


Figure 6. 2: H₂ – TPR of Ni/Ce-Zr and Ni/Ce-Zr@SiO₂

The NH₃-TPD profiles of Ni/Ce–Zr and Ni/Ce–Zr@SiO₂ are presented in Figure 6.3. Both catalysts exhibited multi-stage ammonia desorption, indicating the presence of acid sites with varying strengths. For Ni/Ce–Zr, the peaks were observed in the 100–200 °C region, corresponding to weak acid sites, likely associated with surface hydroxyl groups on the Ce–Zr oxide. In contrast, the Ni/Ce–Zr@SiO₂ showed a broader but less distinct response in this region, suggesting a slightly lower concentration or accessibility of weak acid sites after encapsulation. However, in the 250–350 °C range, the silica-encapsulated catalyst

showed a more pronounced desorption peak, which points to an increase in moderate acid sites. Overall, while the total acidity difference is not pronounced, the silica encapsulation appears to influence the distribution and strength of acid sites, with a shift from weaker to moderately strong acidity. This could improve CO₂ adsorption and contribute to enhanced coke resistance during DRM operation.

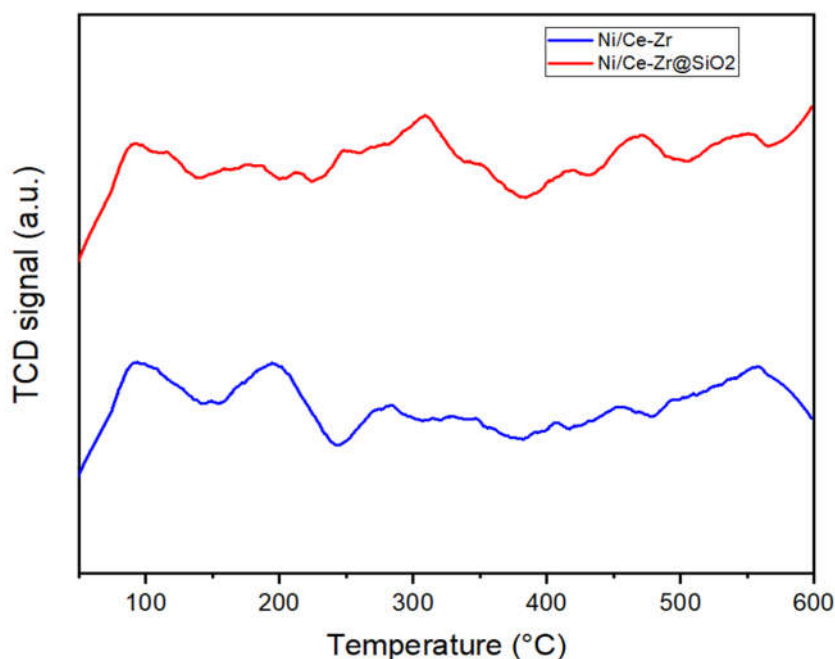


Figure 6.3: NH₃ – TPD profile of Ni/Ce-Zr and Ni/Ce-Zr@SiO₂

6.3 Catalyst activity evaluation

The catalytic activity of Ni/Ce-Zr and Ni/Ce-Zr@SiO₂ was evaluated at varying reaction times, as shown in Figure 6.4a CH₄ conversion and Figure 6.4b CO₂ conversion. In both cases, the catalysts showed high conversions with Ni/Ce-Zr@SiO₂ consistently having higher conversion of CH₄ and CO₂. The conversion increased from 84.8 % at 5 s to 94.6% at 20 s, while Ni/Ce-Zr showed a slightly lower performance, ranging from 79.1% to

86.5%. This improvement can be attributed to enhanced Ni dispersion, stronger metal-support interaction, and better thermal stability provided by the SiO₂ shell. A similar trend was observed in CO₂ conversion. Ni/Ce–Zr@SiO₂ achieved higher conversion values at all time intervals, reaching up to 91.0% at 20 s, compared to 80.1% for Ni/Ce–Zr. The higher CO₂ activation is likely aided by the improved surface acidity facilitated by the Ce–Zr support, further stabilized by the silica layer as confirmed from NH₃-TPD.

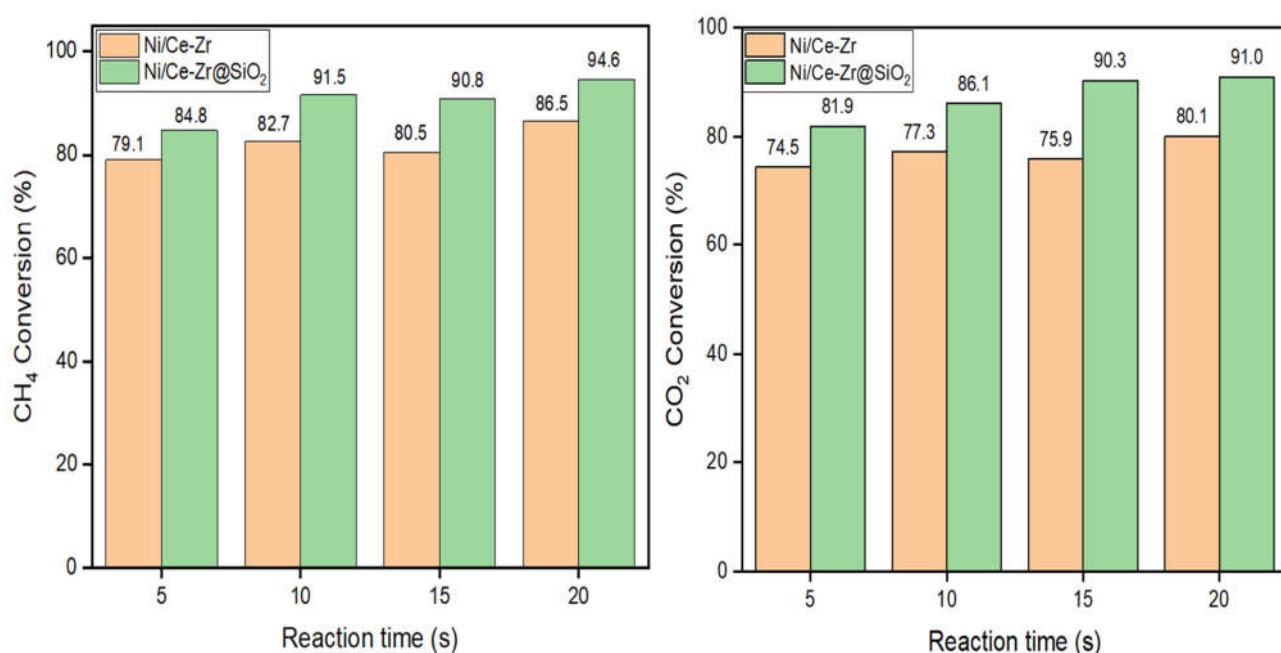


Figure 6.4: Catalytic performance for DRM (a)CH₄ conversion (b) CO₂ conversion

The stability of Ni/Ce–Zr and Ni/Ce–Zr@SiO₂ catalysts was evaluated over 10 consecutive DRM cycles without regeneration, as shown in Figure 6.5. The figure tracks both CH₄ and CO₂ conversions to assess long-term catalytic durability. For Ni/Ce–Zr, a gradual decline was observed, particularly in CO₂ conversion, which dropped from 79% to below 73% by the 10th cycle. CH₄ conversion remained relatively more stable (82–85%) but still showed minor deactivation. This performance loss can be attributed to coke buildup, Ni particle

sintering, or partial loss of active sites, which are common challenges for non-encapsulated systems. In contrast, Ni/Ce-Zr@SiO₂ demonstrated remarkable stability throughout all cycles. Both CH₄ and CO₂ conversions remained consistently high, with CH₄ conversion staying above 89% and CO₂ conversion above 85%. This sustained activity reflects the structural advantage conferred by the SiO₂ shell, which likely prevented Ni sintering and minimized carbon accumulation. These results reinforce that silica encapsulation significantly enhances the catalyst's resistance to deactivation, making it better suited for long-term DRM applications.

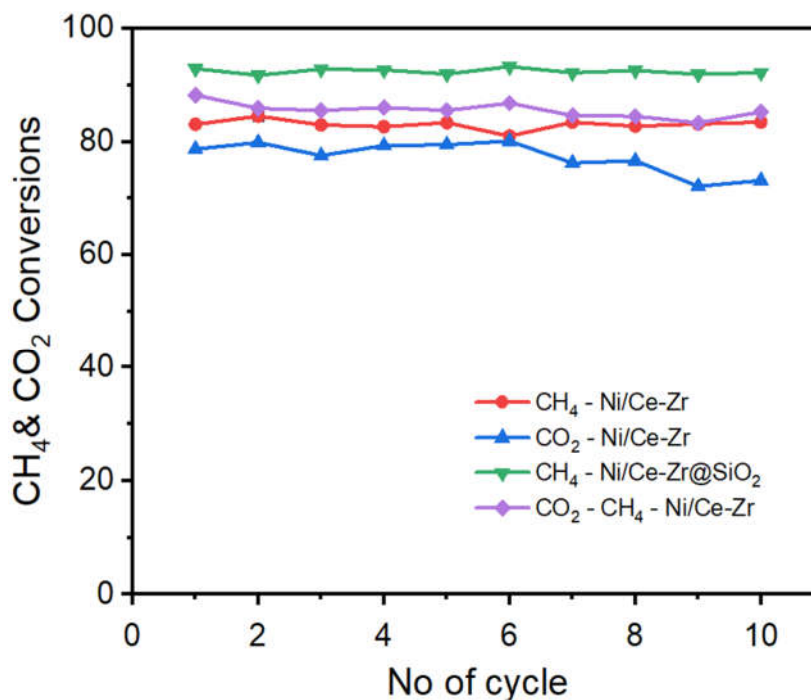


Figure 6.5: Catalyst stability: CH₄ and CO₂ conversions of Ni/Ce-Zr and Ni/Ce-Zr@SiO₂

6.4 Spent catalyst characterization

TEM micrographs of the spent catalysts are shown in Figure 6.6. The Ni/Ce-Zr catalyst (Figure 6.6 a,b) shows irregular and aggregated particles, with visible dark regions

indicating possible Ni particle sintering. The presence of filamentous structures in some regions point to the formation of carbon nanotubes (CNTs), which are known contributors to catalyst deactivation. In contrast, the Ni/Ce–Zr@SiO₂ (Figure 6.6c,d) retains a well-defined spherical core–shell morphology, even after repeated reaction cycles. The SiO₂ layer remains intact, encapsulating the Ni/Ce–Zr core and preventing particle migration or sintering. No significant carbon filaments are observed, indicating that the silica shell effectively suppressed coke formation, likely by limiting CH₄ decomposition on exposed Ni surfaces. These observations confirm the protective role of the SiO₂ shell, maintaining structural stability and extending the catalyst's operational life under DRM conditions.

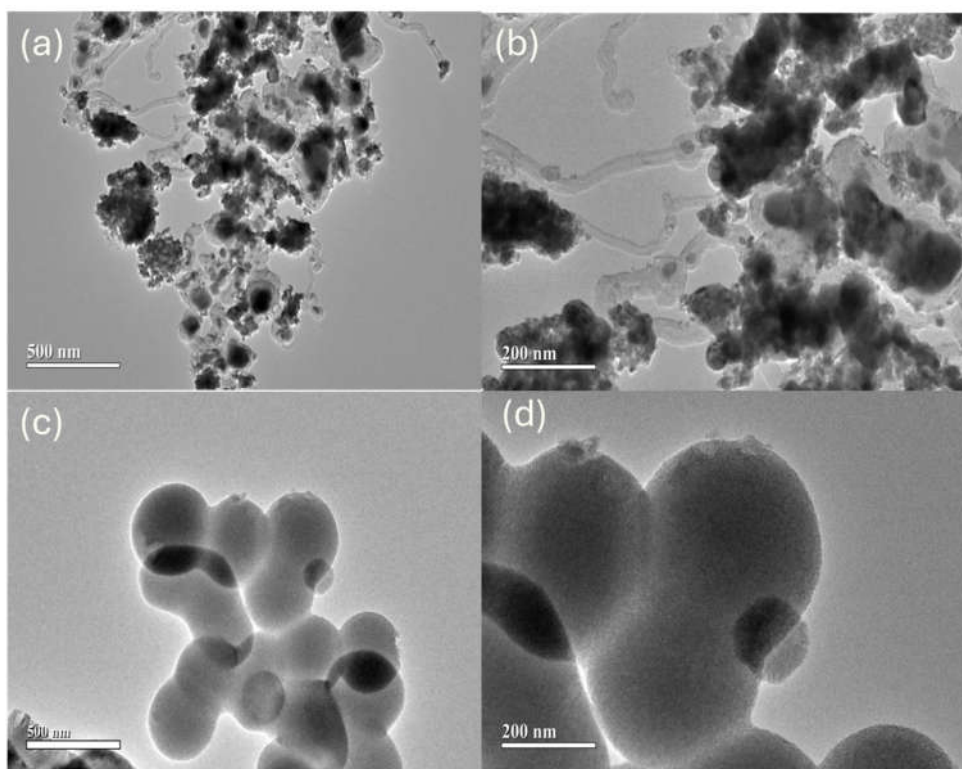


Figure 6.6: presents the TEM of the spent catalysts. (a,b) correspond to Ni/Ce–Zr, while (c,d), corresponds to Ni/Ce–Zr@SiO₂.

The SEM image of Ni/Ce–Zr in Figure 6.7a reveals irregular, block-like particles with rough surfaces, suggesting morphological degradation after reaction. The relatively larger particle size and aggregation may be due to sintering of Ni species during high-temperature DRM. Elemental mapping in Figure 6.7c shows distribution of Ce, Zr, Ni, C, and O, but EDS spectrum Figure 6.7e indicates the presence of intense carbon likely from CH₄ decomposition during DRM reaction, this is in alignment with TEM findings of the visible CNTs on the catalyst surface. In contrast, Ni/Ce–Zr@SiO₂ Figure 6.7b shows a finer, more compact surface with preserved spherical-like features, indicative of the silica shell structure remaining intact. The morphology appears less affected by the reaction, suggesting better resistance to structural collapse. Elemental mapping in Figure 6.7(d) confirms distribution of Ni, Ce, Zr, O, and notably Si, while the EDS spectrum Figure 6.7(f) also shows strong Si peaks, confirming the silica coating remained present after reaction. Furthermore, lower carbon signals in Ni/Ce–Zr@SiO₂ point to reduced coke formation as compared with Ni/Ce–Zr. Overall, the SEM–EDX results further validate the protective effect of the silica encapsulation in preserving catalyst morphology, suppressing

coke formation, and maintaining the active site dispersion during dry reforming.

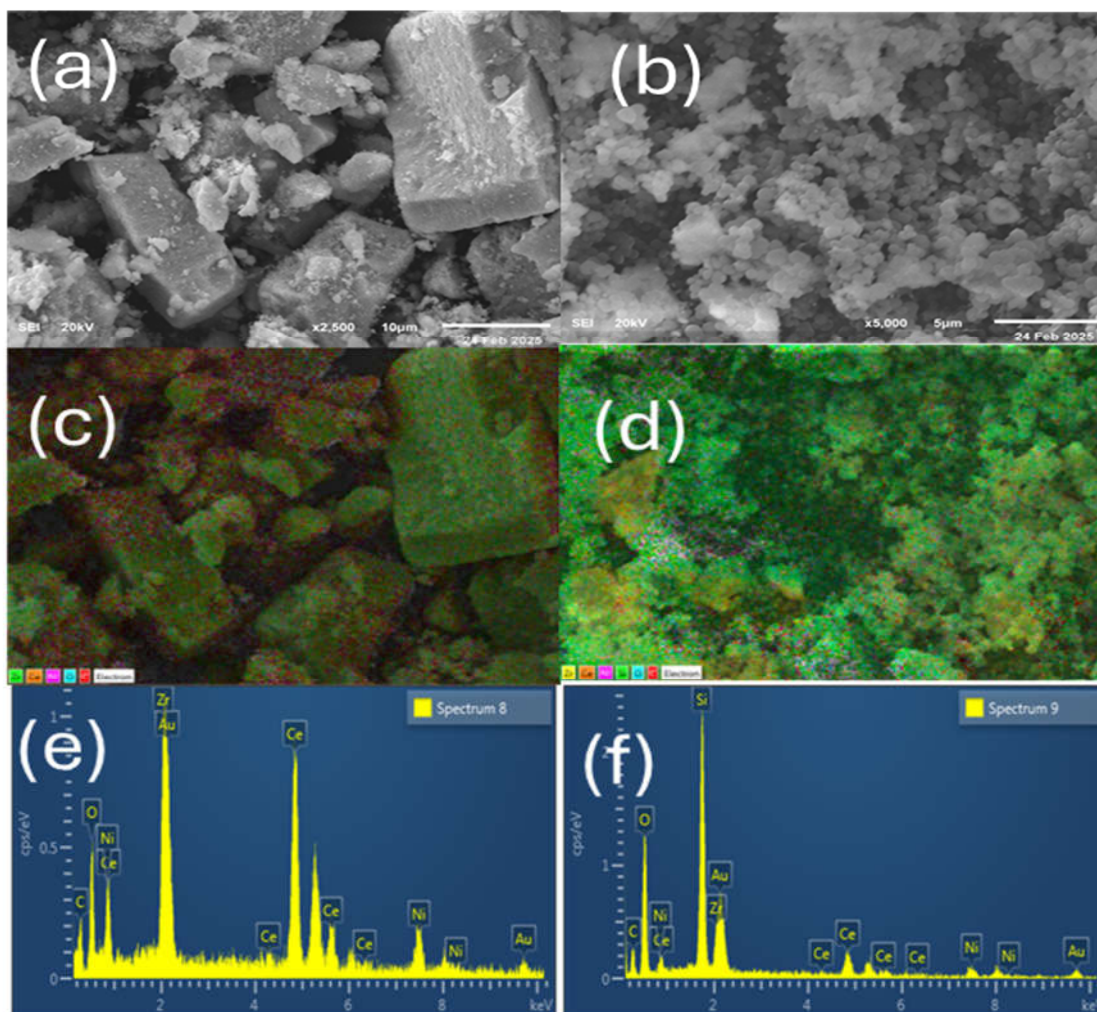


Figure 6.7: SEM images of spent catalyst (a) Ni/Ce-Zr (b) Ni/Ce-Zr@SiO₂ (c) EDS-Mapping Ni/Ce-Zr (d) EDS-Mapping Ni/Ce-Zr@SiO₂ (e) EDS X-ray spectra Ni/Ce-Zr (f) EDS X-ray spectra Ni/Ce-Zr@SiO₂

TGA-DTG analysis (Figure 6. 8) reveals minimal weight loss for both Ni/Ce-Zr and Ni/Ce-Zr@SiO₂ catalysts across the full temperature range, indicating low levels of coke deposition and excellent thermal stability after DRM operation. The absence of significant DTG peaks suggests negligible oxidation of carbonaceous species, further supporting the catalysts' resistance to carbon buildup. This thermal behavior is consistent with their high

stability observed over 10 redox cycles, confirming that both catalysts maintain structural integrity under repeated exposure. The slightly flatter profile of the SiO₂-encapsulated catalyst reflects enhanced Ni stabilization and diffusion control, but both systems demonstrate promising resistance to deactivation, validating their durability under harsh DRM conditions.

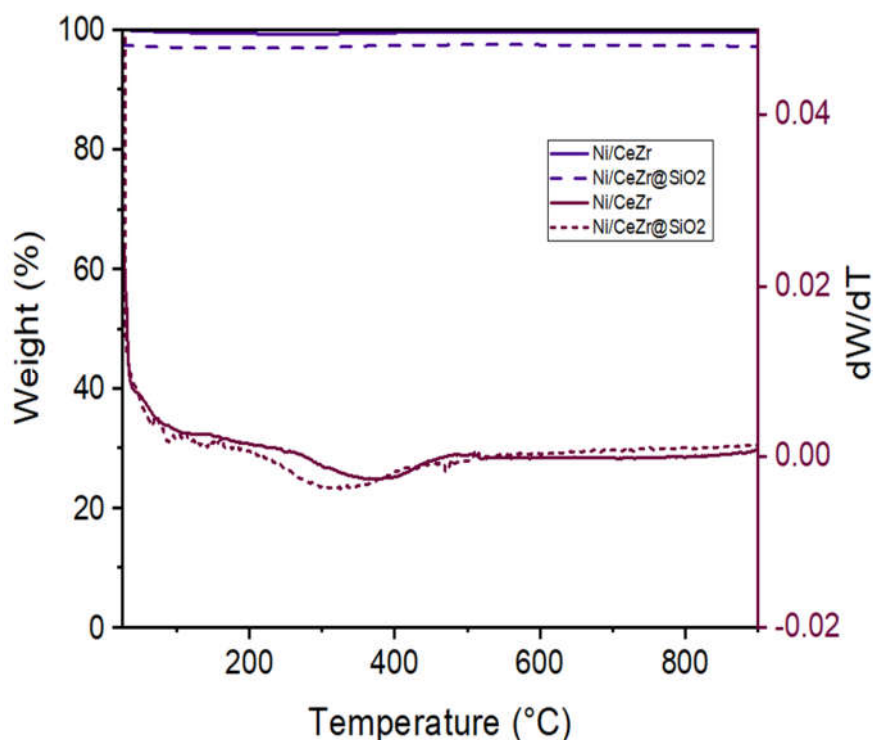


Figure 6. 8: TGA and DTG of spent Ni/Ce-Zr and Ni/Ce-Zr@SiO₂

This chapter presented a detailed study of Ni/Ce–Zr and Ni/Ce-Zr@SiO₂ under DRM. Both catalysts exhibited high activity, but the SiO₂ encapsulated catalyst consistently outperformed the unencapsulated catalyst in terms of CH₄ and CO₂ conversion, product yield, and stability over multiple cycles. Physicochemical characterizations revealed that silica encapsulation improved metal dispersion, enhanced thermal stability, and modified surface acidity. Spent catalyst analyses, including TEM, SEM-EDX, and TGA, confirmed

reduced carbon deposition and preserved morphology in the encapsulated catalyst. In conclusion, Ni/Ce–Zr@SiO₂ demonstrated superior structural integrity and coke resistance, highlighting the effectiveness of the core–shell design strategy for long-term DRM performance.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

Following are salient points that could be inferred from the present study:

- A series of Ni-based catalysts supported on Ce-Al₂O₃, CaO-Al₂O₃, and Ce-Zr were successfully synthesized and evaluated for dry reforming of methane (DRM).
- Each catalyst was further modified via SiO₂ encapsulation using the Stöber method, forming a core-shell structure aimed at enhancing stability and coke resistance.
- Comprehensive characterization techniques (XRD, BET, TPR, NH₃-TPD, SEM, TEM, and TGA) confirmed that silica encapsulation reduced Ni crystallite size, enhanced metal dispersion, and modified surface acidity, while preserving the structural integrity of the catalyst.
- Catalytic performance tests conducted in a CREC riser simulator at 650 °C demonstrated that silica-encapsulated catalysts achieved higher CH₄ and CO₂ conversions, with Ni/Ce-Zr and Ni/Ce-Zr@SiO₂ reaching up to 94.6% CH₄ conversion and 91.0% CO₂ conversion.
- TGA, DTG and SEM EDS mapping indicate minimal coke-formation in both bare- and SiO₂-encapsulated catalyst. However, the coke formation is much less in Ni/Ce-Al₂O₃@SiO₂ as compared to the bare-catalyst.
- Stability tests over 10 consecutive cycles without regeneration revealed that the encapsulated catalysts retained over 95% of their initial activity.

- The results of this work validate the core–shell strategy as an effective approach for improving Ni-based DRM catalysts for DRM.

7.2 Recommendations

At the end of this study, the following are recommended for further study.

- Optimize nickel loading above 5wt% to determine the upper limit of dispersion and activity without compromising stability or increasing coke formation.
- Investigate the use of alternative silica precursors, such as methyl orthosilicate (MEOS), in place of TEOS during encapsulation.
- Conduct detailed kinetic studies of the DRM reaction over both encapsulated and non-encapsulated catalysts to better understand reaction mechanism and influence on activation energy.
- Investigate regeneration strategies for partially deactivated catalysts to assess recyclability and extend catalyst lifespan.
- Model the reactor behavior in Aspen Plus to scale up the system and predict catalyst performance in a flow reactor.

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Hydrogen-Rich Syngas,” *Nanomaterials*, vol. 12, no. 9, 2022, doi: 10.3390/nano12091556.

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Vitae

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RESEARCH INTEREST

- Heterogeneous catalysis for clean energy production
- Bio-based feedstock valorization (e.g., lignin depolymerization to platform chemicals)
- Thermodynamics, kinetics, and machine learning to optimize catalyst performance

ACADEMIC BACKGROUND

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PUBLICATIONS

- Alabi S., Gambo Y., Adamu S., and Hossain M. M., 2025. Chemical Looping: A Sustainable Approach for Upgrading Light Hydrocarbons to Value-Added Olefins. The Chemical Record, DOI: <https://doi.org/10.1002/tcr.202400157>
- Alabi S., Adamu S., Gambo Y., Hossain M. M., and Al-Shammari A. A. Advancements in Catalyst Design for CO₂ Reforming of Methane: Mechanisms, Thermodynamics, Core-shell and Future Prospects. *International Journal of Hydrogen Energy* (Under review)

- Alabi S., Adamu S., Hossain M. M., and Al-Shammari A. A. A Comparative Study of SiO₂ Encapsulated and Unencapsulated Ni/Cao-Al₂O₃ Catalysts for Dry Reforming of Methane. **(Presented at 33rd Annual Saudi-Japan Symposium).**