

Enhanced Photothermal Methane Conversion: Catalysts and Reactor Systems

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Preface

Motivation

وَلَيْسَ أَخُو عِلْمٍ كَمَنْ هُوَ جَاهِلٌ

تَعْلَمُ فَلَيْسَ الْمَرْءُ يُولَدُ عَالِمًا

"Seek knowledge, no one is born a scholar, the one with knowledge is unlike the ignorant."

The above line of poetry by Imam Al-Shafi'ee highlights the profound value of lifelong learning and the transformative power of knowledge. It reflects the merits of perseverance in the pursuit of understanding, serving as a timeless reminder that growth and distinction stem from a commitment to acquiring and applying knowledge. This line is added to reflect the dedication to research as a pathway to making meaningful contributions to society.

The research topic covers the greenhouse effect on our daily life which deems our planet inhabitable. Fossil fuels consumption is one of the main reasons behind the increasing emissions of greenhouse gases. The ruining increase in consumption of the fossil fuels urges alternative sources of energy. Alternative renewable energy sources like solar energy can energize our daily life and maintain sustainable development. It is attractive to use solar energy to produce commodity chemicals and materials that are a life necessity. More appealing is to use the photothermal effect to convert the greenhouse gases. Photothermal reforming of methane proposes the use of the abundant sunlight to energize the highly energy-demanding reforming reactions and produces value-added chemicals. The present work is devoted to studying and maximizing the photothermal conversion of the main greenhouse gases; namely, carbon dioxide and methane to syngas (a mixture of hydrogen and carbon monoxide). Moreover, it proposes employing the disadvantageous temperature gradient of the photothermal effect to drive the valorization of these greenhouse gases to commodity chemicals to the syngas in a single-reactor through successive Fischer-Tropsch reaction. On the other hand, the suppression of this temperature-gradient was dealt with by developing a new design of the photothermal reactor. These studies were conducted in the Graduate School of Human and Environmental Studies, Kyoto University, Japan under the supervision of Prof. Hisao Yoshida and the co-supervision of Dr. Akira Yamamoto.

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This dissertation concludes the author's journey at Kyoto University. However, this is not the end, but rather the start of a new journey towards a better future.

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Abbreviation and symbol list

AQE	Apparent Quantum Efficiency
BRM	Bi-Reforming of Methane
DRM	Dry Reforming of Methane
LSPR	Localized Surface Plasmonic Resonance
NIR	Near Infrared
OCM	Oxidative Coupling of Methane
POM	Partial Oxidation of Methane
SRM	Steam Reforming of Methane
WGS	Water-Gas Shift
Φ	Diameter of the light spot
P	Light power
$\dot{r}_i$	Formation rate of product (i)
$\dot{r}_{syn}$	Sum of CO and H ₂ formation rates ($\dot{r}_{CO} + \dot{r}_{H_2}$)
ΔH°	Standard enthalpy of reaction
η	light-to-fuel conversion efficiency

Chapter 1

General Introduction

Greenhouse Gases

One of the most urgent environmental issues in present time is the rising concentrations of greenhouse gases (GHGs) in the atmosphere. These gases, which are mostly made up of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), trap heat and play a major role in climate change and global warming. Methane, although representing around 19.5 % of GHGs emissions as shown in Figure 1.1, is the one of the most powerful of these, estimated to have a potential for global warming that is around 25 times higher than that of CO_2 . [1] Traditional industrial processes are a significant source of greenhouse gas emissions, especially those that involve the extraction and use of fossil fuels. [2, 3] Carbon dioxide (CO_2) and methane (CH_4) are two of the most significant contributors to greenhouse gases (GHGs), which are the main cause of climate change. [3] CO_2 from burning fossil fuels has garnered a lot of attention as a global necessity and should be held accountable for the threat posed by the greenhouse effect worldwide. [4, 5] Tackling CH_4 and CO_2 emissions across these diverse sources is essential for sustainable environmental management and effective climate mitigation strategies.

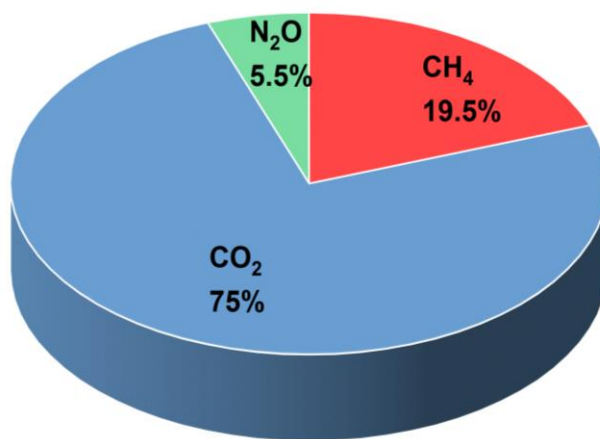


Figure 1.1 Greenhouse Gas emissions by gas (percentages based on Million Metric Ton of CO_2 Equivalent). [6]

Methane has become an increasingly important feedstock in many industrial processes and the main hydrocarbon for domestic energy production because of its abundance and effective

combustion when compared to other fossil fuels. [7] However, mitigation of methane emissions is an essential part of climate action efforts because of its increased impact and its various emission sources. [7] The important sources of anthropogenic CH_4 emissions are multifarious as summarized in Figure 1.2 including: (1) agricultural practices, especially livestock farming, which produces significant amounts of CH_4 through fermentation; (2) waste management processes, where decomposing organic matter in landfills and wastewater treatment facilities releases CH_4 ; (3) biogas production, although a valuable renewable resource, can release methane if improperly managed; (4) and natural gas and oil production, where methane leakage is common. [8, 9]

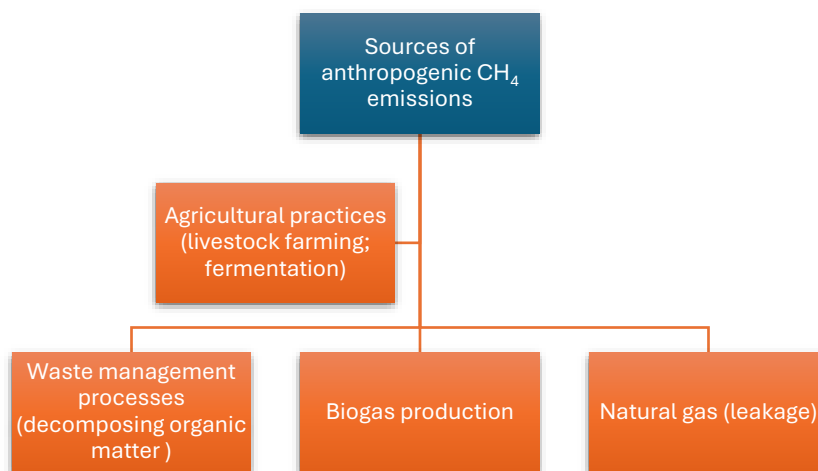


Figure 1.2 Summary of anthropogenic CH_4 sources. [8, 9]

These sources end up in the atmosphere leading to increasing the CH_4 concentration. Global methane and carbon dioxide concentrations rose from 1650 ppb and 345.36 ppm in 1985 to 1884.7 ppb and 412.31 ppm in September 2021, respectively, according to data published by the Earth System Research Laboratory (ESRL).[8, 9] However, much more attention is paid towards the CO_2 capture and utilization (CCU) compared with CH_4 as seen in Figure 1.3. Hence, it would be rational to address CH_4 conversion and valorization through sustainable pathways due to its various emission sources as shown in Figure 1.2 and its increasing concentration. CH_4 can be catalytically converted alone for example in methane pyrolysis or decomposition reaction [10, 11]; or by reacting with other available reactants such as O_2 in methane oxidation [12-14]; or with other GHGs such as CO_2 and steam in methane reforming [9, 15-18]. The advantages and disadvantages of each of these reactions will be discussed and summarized in the following section.

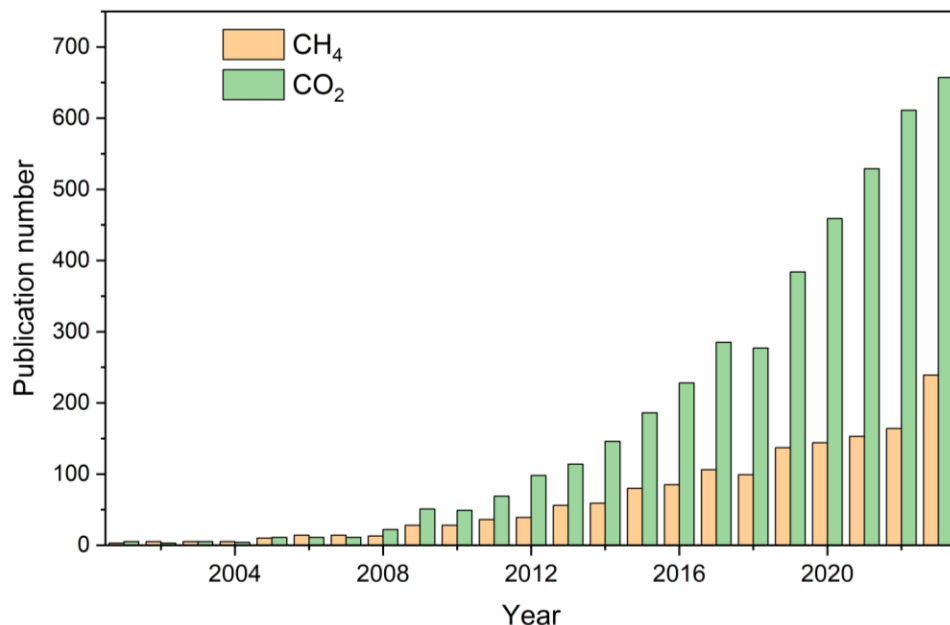


Figure 1.2 Annual publication number on CO₂ and CH₄ capture and utilization obtained from web of science search by “CO₂ capture and utilization” and “CH₄ capture and utilization” on November 6, 2024.

Methane Conversion Pathways

In general, CH₄ conversion can be achieved through several pathways including methane pyrolysis or decomposition [10, 11], methane oxidation (partial [12], total [13], and oxidative coupling [14]) and methane reforming (dry [9, 17, 19], steam[15, 16, 20], or combined [18]).

To start with CH₄ decomposition (eq. 1.1), it has the advantage of producing H₂ and solid carbon. Research was devoted to produce value-added materials like graphite, graphene, or CNT [21]. However, it is challenging to store H₂ in addition to the difficulty to control the yield of C-deposits hinders the large-scale application of this reaction.



CH₄ oxidation presents a good way to obtain H₂-rich syngas as in the partial oxidation case (eq. 1.2), light hydrocarbons as in the oxidative coupling (eq. 1.3 and 1.4) (OCM), or water and CO₂ in the case of complete combustion (eq. 1.5). However, the efficiency of the OCM is limited and requires high energy.[14, 22-24] Besides, the oxidative coupling necessitates the rational control of the O₂ amount otherwise full oxidation would take place causing a higher carbon

footprint. The complete combustion of methane (eq. 1.6) is highly exothermic, providing a significant energy release that can be efficiently harnessed for power generation.[5] However, this reaction also produces a high carbon footprint due to the direct conversion of methane to carbon dioxide, contributing to greenhouse gas emissions and climate change.



Methane reforming reactions convert CH_4 with CO_2 and/or H_2O to produce tunable syngas (CO and H_2).[9, 15-18] The importance of syngas relies in being a valuable platform that had been being used as a feedstock for several other reactions such as Fischer-Tropsch synthesis (FTS) or methanol synthesis.[16, 25, 26] Dry (CO_2) reforming of methane (DRM, eq. 1.7) has the advantage of eliminating two GHGs simultaneously; despite having a relatively H_2 -lean syngas ($\text{H}_2/\text{CO} < 1$) and low catalyst stability.[9, 27, 28] Contrary, steam reforming of methane (SRM, eq. 1.8) has higher H_2/CO ratio around 3-4, and it enjoys high coke resistance in the same time. [29] On the other hand, steam and CO_2 combined reforming; also known as bireforming of methane (BRM) (eq. 1.9) enjoys the merits of tunable H_2/CO ratio and the suppressed coke formation at the same time.[18, 30] In addition, BRM has more tolerance towards the quality or composition of the feed gas (low quality, CO_2 -rich natural gas can be used).[18]



Table 1.1 Summary of CH₄ conversion reactions^[a]

Reaction	ΔH° (kJ/mol)	Products	Advantages	Challenges
CH ₄ decomposition	74.8 (endothermic)	H ₂ and solid carbon	H ₂ production; potential for value-added C-products (graphite, graphene, CNT)	H ₂ storage; controlling C yield
POM	-35.7 (exothermic)	CO and H ₂ -rich syngas	H ₂ -rich syngas; low carbon deposits	Need for controlled O ₂ to avoid over-oxidation
	-281.7 (exothermic)	CO and H ₂	Syngas production; less C deposition	Requires controlled O ₂ to prevent complete combustion
OCM	-281.7 (exothermic)	C ₂ H ₄ and H ₂ O	Light hydrocarbons; limited C-deposition	High energy requirement; complex control of O ₂ levels
	-281.7 (exothermic)	C ₂ H ₆ and H ₂ O	Light hydrocarbons; low C-deposit	Requires careful O ₂ control to prevent CO ₂ production
CH ₄ full oxidation	-802.3 (exothermic)	CO ₂ and H ₂ O	High energy release, useful for power generation	High carbon footprint; CO ₂ emissions
DRM	247 (Highly Endothermic)	CO and H ₂ -lean syngas	Utilizes CO ₂ , reduces greenhouse gas emissions.	Highly Endothermic, prone to catalyst deactivation due to carbon deposition. high CO content syngas less suitable for FTS
SRM	206 (Endothermic)	CO and H ₂ -rich syngas	Commercialized technology, high H ₂ yield, efficient for hydrogen	High H ₂ /CO ratio favors methanation in FTS,

		production; suitable H ₂ /CO ratio for hydrogen applications	requires significant energy; high CO ₂ emissions
BRM	CO and H ₂ (Endothemic syngas	Tolerates high CO ₂ content, H ₂ production; tunable H ₂ /CO ratio for various applications	Requires precise control of CO ₂ /H ₂ O inputs; potential for carbon deposition affects catalyst stability

[a] The data summarized in this table were collected from references [5, 9-11, 15, 18, 31-33]

In this dissertation, we focus on methane dry and bi- reforming to leverage the simultaneous utilization of both CO₂ and CH₄. This is because they are not only commonly present in several feedstocks like biogas and industrial waste gases, but also because they represent two of the most impactful greenhouse gases. In addition, this approach would upgrade these GHGs emissions into valuable products such as syngas, providing a versatile platform for producing chemicals and fuels while contributing to sustainable energy and resource efficiency.[9, 15-18] However, several challenges are associated with methane reforming reactions that can impact efficiency, cost-effectiveness, and environmental sustainability. [9, 15-18] For instance, the high energy demand and catalyst deactivation of these reactions represent the major challenges. The challenge of high energy demand was addressed in several studies leading to proposing the development of other energizing approaches such as microwave-assisted catalysis[34], plasma catalysis[35], and solar catalysis[22]. The solar energy besides being abundant and renewable resource, can induce the photothermal effect by irradiating the catalyst materials to alternate the conventional thermal catalysis.[36-38] We will first distinguish the thermal and solar approaches of energizing the reforming reactions in recent studies. Then, we will discuss the catalysts and their stability, especially in terms of the challenges associated with the photothermally driven reactions.

Approaches for Energizing the CH₄ Reforming Reactions

The conventional way is to use the thermal energy to drive these reactions, but photocatalysis has received significant attention for their potential in energizing catalytic conversions. [36-38] This is due to the intriguing reaction mechanisms the light can stimulate within catalyst materials. In addition, combinations between thermal catalysis and photocatalysis were developed, known as photo-assisted thermal catalysis, to obtain synergism between the merits of thermal heating and light irradiation.[32, 39-42] This interesting synergism motivated several studies to distinguish the contribution of each approach to the overall catalytic reaction rate. [39, 43-45]

Thermal-driven CH₄ reforming reactions are effective in promoting high conversion rates, which is why this approach is the most widely used. Thermal catalysis is convenient for industrial applications because it can be efficiently scaled up to handle high flow rates.[16] However, its dependence on energy from fossil fuels to reach high temperatures cause issues, besides the energy scarcity, such as the contribution to the GHGs emissions. [46, 47]

Photocatalysis, utilizing solar energy to induce catalytic reactions through the interaction of the generated charge carriers with reactants.[32, 48] However, it is hindered by the low light consumption and decreased conversion efficiency, mainly as a result of limited photon absorption and difficulties to produce adequate energy levels only from solar radiation. These limitations restrict the use of photocatalysis in CH₄ reforming.[22, 32]

Light irradiation, such as visible or ultraviolet light, is used in photothermal systems to create electronic excitations in catalysts, which turn light into heat. For instance, metals such as Au, Ag, or Cu exhibit localized surface plasmonic resonance (LSPR), which raises the local temperature and increases the catalysts' surface activity.[22, 32, 45, 49] Free electrons in the metal are excited by incident light in LSPR, creating hot electrons that can pass through the Schottky barrier and catalyze the reaction.

Photothermal approach can be applied to non-plasmonic metals, such as Fe, Ni, Co, Ru, and Rh, can also create heat through visible or infrared irradiation providing sufficient energy to elevate the system's temperature.[22, 32, 45] Recombination of electron-hole pairs through phonon vibration is another pathway in these materials, where thermal energy is produced by carrier

recombination processes like Auger or Shockley-Read-Hall recombination. These methods provide a sustained temperature increase, promoting CH₄ reforming reactions.

External heating (using electric heaters or furnaces) can be used to augment photonic energy to drive the reaction when solar energy alone is insufficient.[50] By combining light-induced electron excitation with extra heat energy, this method—often referred to as photo-assisted catalysis—improves catalytic activity over a broad temperature range. Localized active sites and charge density regions are produced by the combination of solar energy and external heating, which maximizes the CH₄ reforming process.[51]

Table 1.2 Summary of approaches of energizing the CH₄ reforming reactions^[a]

Approach	Energy source	Effective wavelength	Mechanism of Light absorption	Catalyst Material	Advantage	Disadvantage
Thermal Catalysis	Thermal energy (mainly)	-	-	Metal-based catalysts (e.g., Ni, Co)	High conversion, scalable for industrial applications	High energy demand, fossil-fuel-generated heat
Photocatalysis	Light energy	mainly, UV	Bandgap excitation generates electron-hole pairs, interacts with molecular orbitals of adsorbed reactants	Semiconductor (e.g., TiO ₂ , ZnO, etc.)	Environmentally friendly, uses solar energy	Limited light utilization, low conversion efficiency, fast recombination
Photothermal	Light energy		LSPR-induced light	Plasmonic metals	Efficient heat generation via LSPR,	Requires precise control of

UV/V	absorption and	(e.g., Au,	higher local	light intensity
isible/	heat generation	Ag)	temperatures	and stability
NIR	Broad-	Non-	Cost-	No LSPR
	spectrum	plasmonic	efficient,	effects and
	absorption and	metals	tolerance to	prone to
	vibrational	(e.g., Fe,	high	deactivation
	relaxation	Co, Ni,	temperatures,	under
		etc.)	and high	reaction
			activity	conditions

[a] The data summarized in this table were collected from references [22, 32, 43, 45, 49]

Based on their distinct mechanisms of converting light and/or heat to drive CH₄ reforming, these energizing approaches offer distinct advantages in obtaining high CH₄ conversion values. They allow for flexibility in scaling and optimize the reaction efficiency according to available energy resources. Nonetheless, due to their potential to achieve high energy conversion efficiencies, we will compare the thermal and photothermal approaches as our focus.

Thermal CH₄ Reforming

The high temperatures between 650–1250°C and the concomitant coke formation posed challenges against large-scale application of DRM deeming it as an immature pathway to obtain.[9, 36, 52] Meanwhile SRM is considered mature technology with pilot units already operating in the meantime at temperatures between 800–1000°C. [15, 53] Moreover, advances in the renewable energy conversions led to significant advances in this reaction that can generate electricity to energize them. Aarhus university solar-driven power-to-electricity established electrified SRM pilot unit that generates the electricity from renewable energy sources; then this electricity powers the SRM reactor to convert the biogas feedstock to syngas. [54] The merits of this reaction especially the coke resistance in addition to the high H₂/CO are believed to be the main reasons. The BRM, although having the ability to tune the H₂/CO, the tolerance towards the high CO₂ feed, and the intermediary coke resistance compared to DRM and SRM, it is still under-explored and not commercially commissioned.

Photothermal CH₄ reforming

Solar energy has been proposed as a sustainable energy source to drive these reactions, reducing dependency on fossil fuels and potentially lowering the carbon footprint associated with methane reforming. [36-38, 46] The emerging field of photothermal catalysis holds promise for substituting conventional energy sources with concentrated solar energy, providing a more environmentally friendly pathway to drive CH₄ reforming. Since the 1990s, extensive research has explored photothermal catalysis across several key processes,[36] including steam reforming of methane (SRM),[29, 55, 56] dry reforming of methane (DRM), [9, 45, 50, 57-63] that have significant advances in photothermal catalytic systems, however, photothermal bireforming of methane (BRM) remains underexplored. [30] As mentioned earlier, methane reforming reactions are highly endothermic, requiring substantial temperatures to achieve considerable CH₄ conversion levels.[64] Typically, this can be achieved by focusing the light which in turn produces uneven distribution of the photon flux within the catalyst volume leading to higher temperatures where photon flux is high and lower temperatures where the photon flux is lower. [29, 42, 46, 48, 65-67] Given the huge potential of photothermal CH₄ reforming, we will briefly cover the related studies mentioning the temperature gradient and discuss the possible approaches to deal with it.

The Effect of Temperature Gradient on Photothermal CH₄ Reforming

The temperature gradient, induced during the photothermal reactions within the catalyst bed, had generally posed a significant challenge in photothermal catalysis. [29, 42, 46, 48, 65, 66, 68] This is because the low-temperature zone(s) can promote the reverse reactions or undesirable side reactions. In trials to remove this low-temperature zones, in most cases, researchers tended to combine the light irradiation with external heating to obtain high conversions in light-assisted reactions.[50] The involvement of external heating necessitates energy sources including the fossil fuels that would increase the GHGs emissions.[38] Since we aim to maximize the use of the renewable solar energy to replace the fossil fuels, we will discuss the characteristics of the temperature gradient as a major setback to enhance the photothermal CH₄ conversion.[29] First, it would be beneficial to determine the influence of the temperature gradient on the photothermal CH₄ reforming. This would provide valuable information on how to overcome the shortcoming of the low conversion in the photothermal catalytic reactions, especially for the highly endergonic

CH₄ reforming reactions. Moreover, investigating this phenomenon could acquaint us with necessary knowledge to maneuver its limitations or provide suggestions on how to eliminate it.

Making use of the temperature gradient

The temperature gradient feature can be utilized to promote the reaction rate.[67] In that study, the NH₃ synthesis rate was enhanced with the formation of a negative gradient. The photothermally-induced temperature gradient can be proposed to efficiently combine reactions that proceed under different temperatures in a single reactor like tandem catalysis process. Tandem reactions combine two or more reaction mechanisms in one reactor, which would substantially save time and cost. [69, 70] Presumably, the temperature gradient can be utilized to combine reactions of different operating temperatures to efficiently develop tandem catalysis system. This offers a sustainable pathway, utilizing low-cost, abundant CO₂ and CH₄ feedstocks like biogas to obtain not only synthesis gas, but also convert this syngas to higher value-added products.

Eliminating the temperature gradient

From another perspective, the temperature gradient could be better eliminated for the sake of maximizing the conversion in CH₄ reforming. The elimination of the temperature gradient would possibly lead to the suppression of the reverse and side reactions. [64] Minimizing the temperature gradient ensures more uniform heating across the catalytic surface, promoting forward reaction rates and improved yield.[71] Additionally, controlling the temperature profile within the reactor helps prevent localized hot spots, which can cause catalyst deactivation and reduce long-term stability in industrial applications. [9, 71, 72]

Catalyst requirements for photothermal CH₄ reforming

Given the endothermic nature of the CH₄ reforming reactions, they require very high temperatures to proceed in considerable conversion rates. This in turn requires maximal light absorption to assure the generation of sufficiently high temperatures that can be generated by focusing the solar light. [36, 64, 73, 74] Several technologies have been developed for the efficient maximizing the incident light intensity over the catalyst volume.[64, 75] However, the inherent temperature gradient poses another challenge for the catalyst stability.[71] This gradient comprises a very high-temperature zone as well as a low-temperature zone. Although the high temperatures

would benefit the reaction rate and the conversion values, they can significantly compromise the catalysts stability causing the catalyst nanoparticles to sinter into larger aggregates.[27] On the other hand, the low-temperature zone shunts the selectivity of the catalyst metal nanoparticles to other less endothermic or even exothermic side reactions. These reactions can occur to either the reactants feed or to the products once they are formed at the high-temperature zone and pass through the low-temperature zone.[29] For instance, the most deleterious example of the less endergonic reactions than CH₄ reforming is the CH₄ decomposition (eq. 1.1) as it generates H₂ and solid carbon deposits. Besides, the formed syngas from CH₄ reforming can undergo other side reactions such as CO disproportionation (also known as Boudouard reaction, eq. 1.11), or CO hydrogenation (eq. 1.12) that can lead to significant C- deposition. Moreover, a huge variety of side reactions can occur between the unreacted reactants and the formed products including water-gas shift (WGS, eq. 1.13), or its reverse reaction (RWGS, eq. 1.10), or CO₂ hydrogenation (eq. 1.14).



In summary, the challenges posed against the catalyst stability and stable catalytic performance are much higher under the photothermal reaction conditions compared to their thermo-catalytic counterparts. This originates mainly from the nonhomogeneous temperature distribution.

Ni-based catalysts have been widely studied for thermo-catalytic dry reforming of methane (DRM) due to their cost-effectiveness compared to precious metals. [9, 17, 76] Previous studies have shown that optimizing Ni nanoparticle sizes—particularly below 7 nm—can effectively reduce coke formation, a significant challenge in DRM.[77-80] Alloying, especially with Co to form Co–Ni alloys, further enhances performance by reducing particle size and altering surface properties, which collectively improves coke resistance. [50, 81, 82] However, issues with coke formation and sintering persist on supported Co–Ni nanoparticles challenges, silica (SiO₂) coatings have emerged as a promising solution. Studies indicate that a porous SiO₂ layer on Ni surfaces not only modifies the surface properties to inhibit coke formation but also physically isolates Ni

nanoparticles, reducing sintering during both thermal and photothermal DRM reactions. [9, 63, 83-85] This approach has proven effective in stabilizing Ni catalysts by limiting unwanted carbon deposition.

Table 1.3 Summary of some selected catalysts used in photothermal CH₄ reforming studies

Catalyst Support Amount (mg)	Reaction conditions	Feed ^[a]	Conversion (%)		Efficiency (%) ^[b]	Reference
			CH ₄	CO ₂		
Cu _{19.8} Ru _{0.2}	$P = 19.20$	$F_{\text{CH}_4} = 20$	56-58	-	AQE =	[51]
Al ₂ O ₃ + MgO 1.5	$\Phi = 2$ mm Full spectrum (Supercontinuum Laser)	$F_{\text{CO}_2} = 20$			16	
Ni ₁ Co ₁	$P = 44.56$	$F_{\text{CH}_4} = 44$	55	63	$\eta = 33.8$	[62]
Al ₂ O ₃ + MgO 20.0	$\Phi = 6$ mm Full spectrum (Xe)	$F_{\text{CO}_2} = 45$				
Ni ₃ Fe ₁	$P = 3.62$	$F_{\text{CH}_4} = 19$	-	-	-	[60]
Al ₂ O ₃ 5.0	Full spectrum (Solar)	$F_{\text{CO}_2} = 19$ $P = 1.8$ Atm				
Ni SiO ₂ 24.3	$P = 34.36$	$F_{\text{CH}_4} = 14$	47	47	$\eta = 12.5$	[86]

[a] F : flowrate (mL min⁻¹), [b] η : light-to-fuel efficiency, AQE: apparent quantum efficiency as reported by the authors.

Table 1.4 Summary of catalysts used in Light-assisted with external heating CH₄ reforming studies

Catalyst Support Amount (mg)	Temperature and light Condition	Feed	Conversion (%)		Reference
			CH ₄	CO ₂	
Ni	$T = 350\text{ }^{\circ}\text{C}$	$F_{\text{CH}_4} = 2.5$	-	-	[45]
CeO ₂ -CePO ₄	$P = 4.81$	$F_{\text{CO}_2} = 2.5$			
	Full spectrum (Xe)				
1.2Ni-0.3Co	$T = 700\text{ }^{\circ}\text{C}$	$F_{\text{CH}_4} = 9.6$	-	91.60	[50]
SiO ₂	$P = 9.00$	$F_{\text{CO}_2} = 9.6$			
30.0	Full spectrum (Xe)				
Ni	$T = 600\text{ }^{\circ}\text{C}$	$F_{\text{CH}_4} = 10.0$	48.70	44.74	[87]
TiO ₂	$P = 3.10$	$F_{\text{CO}_2} = 14.0$			
Ni@SiO ₂ -Yolk	$T = 550\text{ }^{\circ}\text{C}$	$F_{\text{CH}_4} = 10.0$	2.35	3.02	[84]
SiO ₂	$P = 1.07$	$F_{\text{CO}_2} = 10.0$			
30.0 (Ni metal)	Full spectrum (Xe)				
Pt-Si	$T = 600\text{ }^{\circ}\text{C}$	$F_{\text{CH}_4} = 1.4$	4.70	15.00	[88]
CeO ₂	$T = 600\text{ }^{\circ}\text{C} + \text{Full}$	$F_{\text{CO}_2} = 1.4$	24.00	25.00	
10.0	spectrum (Xe)				

Research Objectives and Scope of the Dissertation

In this dissertation, we generally aim to contribute to the enhancement of photothermal CH₄ catalysis to increase its viability. We will first address the catalyst stability and optimizing the irradiation conditions. Then, will try to utilize the photothermally induced temperature gradient can combine reactions of completely different operating temperatures to efficiently develop tandem system. The photothermal-induced gradient can promote two or more reactions simultaneously by creating appropriate temperature zones. This would overcome the thermodynamic limitations of these reactions that makes it impossible for such a tandem reaction to proceed effectively in one uniformly heated reactor. Finally, we will address a key aspect of

photothermal DRM which is the reactor design to minimize non-uniform temperature distribution and enhancing CH₄ conversion efficiency. Unlike previous designs that focused primarily on energy efficiency or other criteria, we aim to facilitate systematic comparisons across catalytic criteria, achieving significantly improved CH₄ conversion values.

To achieve these goals, we aim to:

- (1) Develop stable and resilient catalysts capable of withstanding harsh conditions, particularly the significant temperature gradients encountered in photothermal catalysis of methane reforming.
- (2) Investigate and optimize the composition and structure of Co–Ni alloy multi-yolk@SiO₂ catalysts for enhanced catalytic activity and durability under photothermal conditions.
- (3) Explore possible approaches to maneuver the inherent temperature gradients during photothermal catalysis.
- (4) Explore the potential of utilizing the temperature gradients to induce beneficial side reactions
- (5) Minimize the temperature gradients to enhance the primary reforming reaction through new reactor design.

Scope: In this dissertation, we focused on the synthesis, characterization, and experimental evaluation of novel catalysts designed for photothermal methane reforming. We also examined the temperature gradient, proposing methods to either maximize and exploit or mitigate these effects to obtain better catalytic performance in photothermal catalysis.

Thesis layout

In this thesis, we outline the environmental impact of methane, the potential of photothermal catalysis, and the challenges posed by temperature gradients. In the introduction, we are providing background information, the statement of the problem, and a summary of the research objectives.

In chapter 2, we address the catalyst stability and describe the synthesis of Co-Ni alloy nanoparticles with a multi-yolk structure and their encapsulation within a gas-diffusive SiO₂ shell. We detail the optimization of the Co-Ni ratio and evaluate the catalytic performance under different conditions.

In chapter 3, we investigate the use of temperature gradients to maximize the efficiency of tandem catalysis. In this chapter, we discuss how this gradient can be harnessed to induce beneficial side reactions like Fischer-Tropsch Synthesis, thereby integrating two reaction mechanisms in single reactor.

In chapter 4, we focus on minimizing the temperature gradients, thus stabilizing the primary methane reforming reaction and suppressing undesirable side reactions. In this chapter, we discuss experimental results, comparing different reactors to manage the temperature gradient and its impacts on catalyst performance.

In chapter 5, we summarize the key findings of the research, discuss the implications of these findings in the context of photothermal catalysis, and propose directions for future research. This chapter also focuses on the potential applications and the environmental benefits of the developed photothermal technologies.

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Chapter 2

Photothermal Dry Reforming of Methane on Yolk-Shell Co–Ni Alloy@SiO₂ catalyst

Abstract

Photothermal dry reforming of methane (PT-DRM) is an appealing pathway to convert carbon dioxide and methane into synthesis gas, a mixture of carbon monoxide and hydrogen, via photothermal heating induced by concentrated sunlight. Coke formation and sintering of active metal nanoparticles, however, are a key issue for catalyst stability. In the present study, we demonstrated Co–Ni alloy nanoparticles encapsulated with a porous SiO₂ shell exhibited improved catalytic activity and stability for PT-DRM using visible/near-IR light irradiation without any other external heating. The addition of a tiny amount of Co (1–5 mol% relative to total metal) and SiO₂ encapsulation enhanced the stability by simultaneously suppressing coke formation and sintering of the metal nanoparticles. Furthermore, we revealed that the position of the light irradiation spot has a crucial role in the conversions of methane and carbon dioxide and product selectivity, presumably due to large temperature gradient under the light irradiation. These findings would contribute to designing for effective PT-DRM catalysts with improved activity and enhanced resistance for both coke formation and sintering and emphasize the significant contribution of the temperature gradients to the performance in PT-DRM.

Introduction

The utilization of CO₂ has garnered significant attention for controlling the net CO₂ emission into the atmosphere. Solar-to-fuel technology is a promising route for CO₂ conversion and utilization.[1-4] Among such technologies, solar dry reforming of methane (DRM, eq. 2.1) converts CO₂ with CH₄ into synthesis gas (a mixture of CO and H₂), which serves as an important feedstock for C1 chemistry.[5] The DRM reaction is highly endothermic, and thus requires high reaction temperatures (> 600 °C) to achieve sufficient conversions of CO₂ and CH₄.[6, 7]



In the photothermal approaches, solar energy is used to heat the catalyst and drive the endothermic DRM reaction, resulting in the storage of the solar energy as chemical energy in the form of synthesis gas.

Various studies have been devoted to the development of materials and elucidation of the mechanisms for both thermo-catalytic [3],[8] and light-assisted DRM[9-19] reactions. One crucial issue that has been investigated is catalyst stability, which can be compromised by coke formation and sintering of metal nanoparticles. From a thermodynamic standpoint, coke formation is favored at low temperatures,[7] where it leads to severe deactivation by poisoning catalytic active sites. On the contrary, the sintering of metals is more likely at high temperatures. In the photothermal DRM (PT-DRM) reaction, concentrated sunlight typically generates a catalytic reaction field with a large temperature gradient across the reactor due to the non-uniform light distribution,[20, 21] thus requiring catalytic materials that are highly resistant to both coke formation and sintering over the wide temperature range.

Ni-based catalysts have been extensively investigated for the thermo-catalytic DRM reaction due to the lower cost than precious metals. Numerous studies have reported improvements in resistance to coking and sintering.[22-29] It is well known that the preparation of Ni nanoparticles with a diameter of <7 nm can suppress the coke formation.[22, 30, 31] Fabrication of alloy metal nanoparticles was also proved to be effective, and among them, Co–Ni alloying is known to lead to a decrease in particle size and change the surface property, which improves coke resistance.[32-34] Nevertheless, the coke formation and sintering can occur on the supported Co–Ni nanoparticles catalyst.[35]

In other approaches, porous SiO₂ coatings have been reported as a viable approach to improve resistance against coke formation and sintering.[35] It has been reported that the addition of small amounts of silica to the Ni surface effectively mitigates carbon deposition in both thermal[35] and photothermal[36] DRM reactions. In other words, the SiO₂ coating has the suppressive effects against coke formation by changing the surface properties of Ni and sintering by spatially isolating Ni nanoparticles.[37] Conversely, excessive SiO₂ coating of the active metal has been reported to have a negative impact on the thermo-catalytic DRM reaction, possibly due to suppression of the gas contact with metal particles, and typically, a SiO₂ coating thickness of about 10 nm is optimal.[38] In terms of the gas contact, SiO₂ coatings with internal void spaces between the metal particle and SiO₂ shell have been shown to be effective for DRM.[36, 38-42]

Based on this background, we hypothesize that Co–Ni alloy nanoparticles coated with gas-diffusive SiO₂ shells with the void space are a promising strategy to improve resistance against coking and sintering. Recently, Cai and coworkers reported the preparation of Ni nanoparticles encapsulated with SiO₂ yolk-shell for photothermal CO₂ hydrogenation by a hydrothermal method.[43] By modifying the preparation protocol, in the present work, we successfully synthesized yolk-shell Co–Ni alloy nanoparticles covered with a porous SiO₂ with void spaces around the metal alloy nanoparticles. Moreover, we revealed that the conditions of light irradiation have a significant role in the performance of PT-DRM. Using the optimized catalytic material and light conditions, we demonstrated highly active and stable photothermal DRM systems without external heating.

Experimental

Catalyst Synthesis

Synthesis of Hexagonal Nanoplatelets of Co–Ni Hydroxide

Hexagonal nanoplatelets of Co–Ni hydroxide were synthesized based on the hydrothermal method as reported by Cai and coworkers[43] with some modifications. Briefly, Co(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O (4 mmol of total metal ions) were dissolved in deionized water (DIW, 20 mL). The molar percentage of Co to total metal amount (sum of Co and Ni) was varied in 0, 1, 5, 12.5, 25, 50, and 100 mol%. The solution containing metal cations was added to polyvinylpyrrolidone (2 g) dissolved in DIW (150 mL), and then, 1 mol L⁻¹ NaOH aqueous solution (20 mL) was injected

dropwise for 30 min under Ar flow. The suspension was instantly transferred to a 300 mL Teflon-lined autoclave, and heated at 150 °C for 6 h. The precipitate was washed with DIW through decantation three times.

Encapsulation with SiO₂

The nanoplatelets of Co–Ni hydroxide were encapsulated with SiO₂ using the sol-gel method [43], where the total amount of the metals was 10 wt%. The obtained precipitate of Co–Ni hydroxide was dispersed in a mixture of DIW (100 mL), ethanol (200 mL), and 28% ammonia aqueous solution (10 mL). Tetraethyl orthosilicate (7.7 mL) was added to the suspension under vigorous stirring. After 1 h, the precipitate was collected by centrifugation at 5000 rpm and washed three times with ethanol-DIW mixture (1:1), followed by washing once with DIW. To introduce mesopores into the SiO₂ shell, a hot etching treatment was performed.[43] The precipitate was suspended in DIW (100 mL) in a reagent bottle and then heated it to 100 °C for 1 h. After the hot etching treatment, the precipitate was collected by centrifugation, washed by DIW once, and dried at 80 °C. The obtained powder was calcined at 500 °C for 1 h at a heating rate of 10 °C min⁻¹. The prepared SiO₂ encapsulated Co–Ni catalysts were referred to as Co_xNi_{100-x}@SiO₂ using a molar percentage of Co (x mol%) to the total metal. For comparison, SiO₂-supported Co–Ni catalysts were prepared by wet impregnation with and without citric acid and denoted to Co_xNi_{100-x}/SiO₂ and Co_xNi_{100-x}/SiO₂-CA, respectively.

Characterization

UV–visible–near-IR diffuse reflectance spectra (UV–Vis–NIR DRS) were obtained on a V-570 (JASCO, Japan) using a BaSO₄ plate for the baseline. Powder X-ray diffraction (XRD) was obtained on a LabX XRD-6000 (Shimadzu, Japan) using Cu K radiation. The crystallite size of metal was estimated from the diffraction peaks at $2\theta = 44.5^\circ$. TEM measurements were performed on a JEM-2100F (JEOL, Japan). High-angle annular dark field scanning TEM (HAADF-STEM) and elemental mapping was performed on a JEM-ARM200F (JEOL, Japan). The amount of deposited coke after 2 hours of PT-DRM reaction test was determined using the elemental analysis with CNH analyzer (MT-5 and MT-6, Yanaco Analytical Systems, Japan) and Micro analyzer (JM-10 and JM-11, J Science Lab, Japan). Hydrogen temperature-programmed reduction (H₂-TPR) was conducted by a home-made device with a quartz tube cell and BELMASS mass spectrometer (MicrotracBEL, Japan) from 25 to 800 °C under a gas flow of 5% H₂/Ar (30 mL min⁻¹). BEL-

MAX-G (Microtrac BEL, Japan) was employed to obtain the adsorption-desorption isotherms. The porosity of the catalysts was evaluated using Barrett–Joyner–Halenda (BJH) method. Metal compositions of pelletized samples were determined by an inductively coupled plasma mass spectrometry (iCAP TQ, Thermo Fisher Scientific, Germany) connected to a femtosecond laser system with a galvanometric scanner (Jupiter Solid Nebulizer, ST Japan INC., Japan). NIST (SRM 610 and 612) and USGS reference glasses (GSA-1G and GSE-1G) were used to calibrate the weight abundance of Si, Ni and Co.

Catalytic Activity Test

The photothermal and thermo-catalytic activity tests were performed using a fixed-bed continuous-flow system at ambient pressure represented in Figure 2.1. The catalyst powder was pelletized at 40 MPa and crashed to granules at a diameter of 150–300 μm . The catalyst granules (0.3 g) were added into a flat quartz reactor (20 mm $\times$ 20 mm $\times$ 1 mm, Figure 2.1). Before the catalytic activity tests, the catalyst was heated at 450 $^{\circ}\text{C}$ under an Ar flow, followed by oxidation for 30 min under an O_2 gas flow (100%, 5 mL min^{-1}). Then, the catalyst was reduced by 5% H_2/Ar gas (100 mL min^{-1}) at 600 $^{\circ}\text{C}$. After cooling under the Ar flow, the reactant feed gas (10% CH_4 /12.5% CO_2 /5% N_2 /Ar) was introduced to the reactor at a total flow rate of 200 mL min^{-1} . A 300 W Xe lamp coupled with a 435 nm cut-off filter and a focusing lens was used for light irradiation in PT-DRM reaction test.[21, 44] The irradiated light power was measured using a thermal power sensor (S425C-L, Thorlabs Inc., USA). The power (P) and spot size (Φ) of the irradiated light spot were changed by varying the current value of the power supply and the distance between the light source and reactor, respectively. The light irradiation conditions in the present study were summarized in Table S1. In the thermo-catalytic activity test without light irradiation, the catalyst granules (50 mg) were filled in a quartz tube reactor (inner diameter: 4 mm) and heated by a tubular electric furnace. CH_4 and CO_2 conversions, carbon balance, and light-to-chemical conversion efficiency (η) were calculated using equations 2.2–2.5.

CH_4 and CO_2 conversions and carbon balance were calculated as follows:

$$\text{CH}_4 \text{ conversion (\%)} = ([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}})/[\text{CH}_4]_{\text{in}} \times 100 \quad (2.2)$$

$$\text{CO}_2 \text{ conversion (\%)} = ([\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}})/[\text{CO}_2]_{\text{in}} \times 100 \quad (2.3)$$

$$\text{Carbon balance} = ([\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}})/([\text{CO}_2]_{\text{in}} + [\text{CH}_4]_{\text{in}}) \times 100 \quad (2.4)$$

where $[X]_{\text{in}}$ and $[X]_{\text{out}}$ are the concentrations of X ($X = \text{CH}_4$, CO , or CO_2) in the inlet and outlet gases, respectively. The following equation was used to calculate the light to chemical conversion efficiency (η):

$$\eta (\%) = [r(\text{H}_2)\Delta_c H^\circ(\text{H}_2) + r(\text{CO})\Delta_c H^\circ(\text{CO}) - r(\text{CH}_4)\Delta_c H^\circ(\text{CH}_4)] / P \times 100 \quad (2.5)$$

where $r(Y)$ and $\Delta_c H^\circ(Y)$ are conversion/production rates and combustion enthalpies of Y ($Y = \text{H}_2$, CO , or CH_4), respectively. P is the irradiation power of light (W).

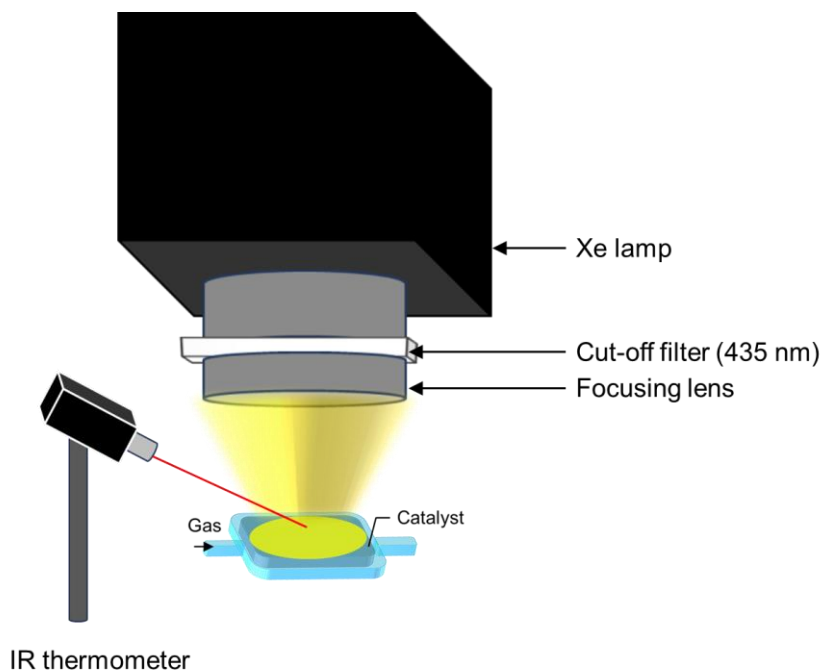


Figure 2.1 Illustrative diagram of the set-up used to conduct the photothermal activity tests

Results and Discussion

Characterization

First, we characterized the Co–Ni samples during the preparation steps. After the hydrothermal treatment, hexagonal nanoplatelets of Co–Ni hydroxides were formed with a lateral size of 25–40 nm and a thickness of 8–12 nm (Figure 2.2a). After SiO₂ encapsulation and hot etching treatment, the hexagonal structure of hydroxides persisted based on the TEM image (Figure 2.2b).

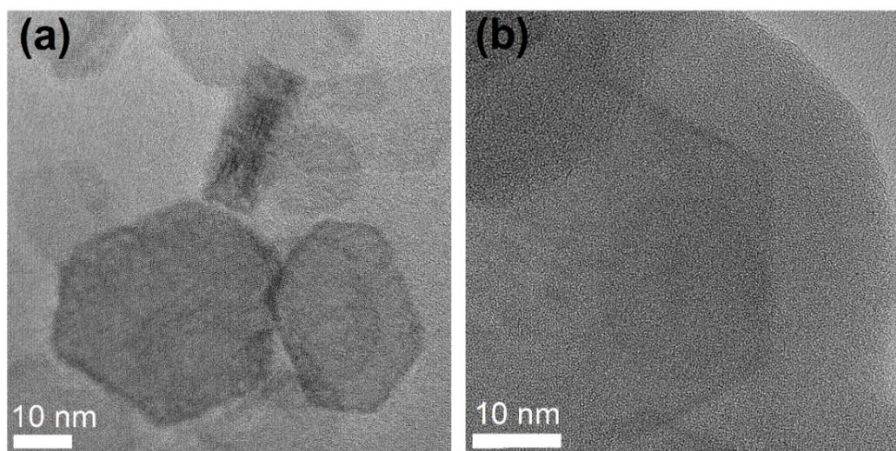


Figure 2.2 (a, b): TEM images of Co–Ni hydroxide nanoplatelets after hydrothermal treatment (a) and after SiO₂ encapsulation (b) in the preparation steps of Co₅Ni₉₅@SiO₂.

Upon the calcination at 500 °C, the XRD patterns indicate that the inner hydroxides changed to their corresponding oxide phases (Figure 2.3). In the monometallic samples (*i.e.*, Ni₁₀₀@SiO₂ and Co₁₀₀@SiO₂), the calcination transformed the Ni and Co hydroxides to NiO and Co₃O₄, respectively. For the Ni-rich samples, the XRD patterns were similar to that of Ni₁₀₀@SiO₂. However, over 50 mol% of Co, another phase became dominant at $2\theta = 18.9, 31.3, 36.8, 44.1, 59.3$ and 65.2 degrees, which is assignable to Co₃O₄ or the solid solution of Co₃O₄-Ni₃O₄[45].

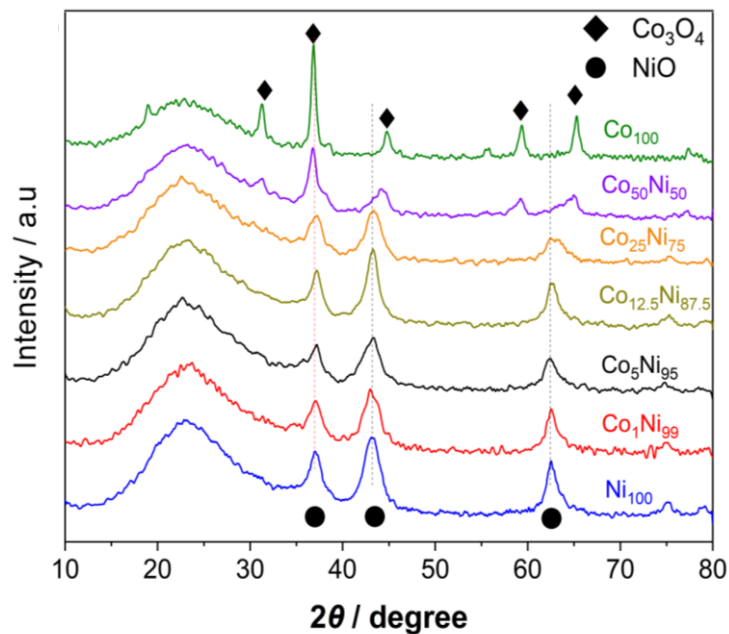


Figure 2.3 XRD patterns of $\text{Co}_x\text{Ni}_{100-x}@\text{SiO}_2$ samples after oxidation at 500 °C.

For the reduction pretreatment of the catalysts, we confirmed that the Co and Ni oxides phase was reduced at < 600 °C by H_2 -TPR (Figure 2.4).

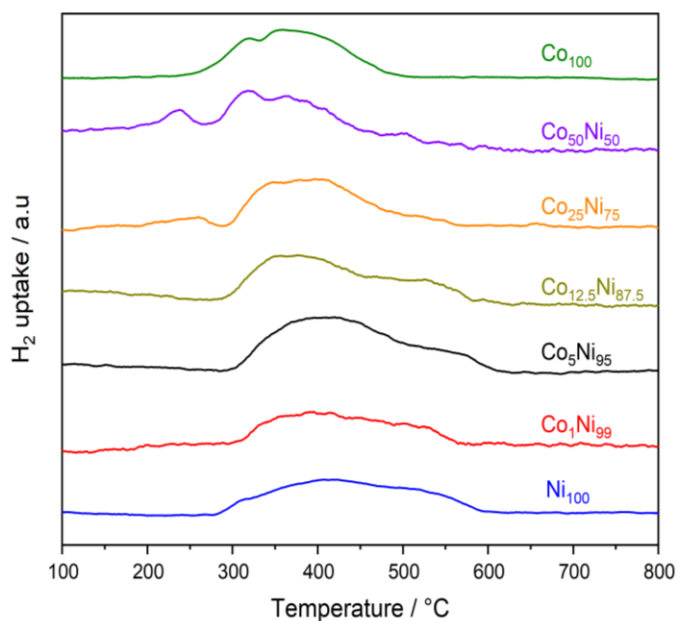


Figure 2.4 H_2 -TPR spectra of the $\text{Co}_x\text{Ni}_{100-x}@\text{SiO}_2$ samples after the calcination at 500 °C

After the reduction treatment at 600 °C, Ni and Co oxides were converted to their metallic phases (Figure 2.5). The three peaks at $2\theta = 44.5$, 51.8 and 76.4° shifted toward lower angles with increasing the Co amount. The change in a lattice spacing calculated from the peaks at $2\theta = 44.5$ showed a positive relation against Co content (Figure 2.6), indicating that Co–Ni alloy nanoparticles were formed after reduction.

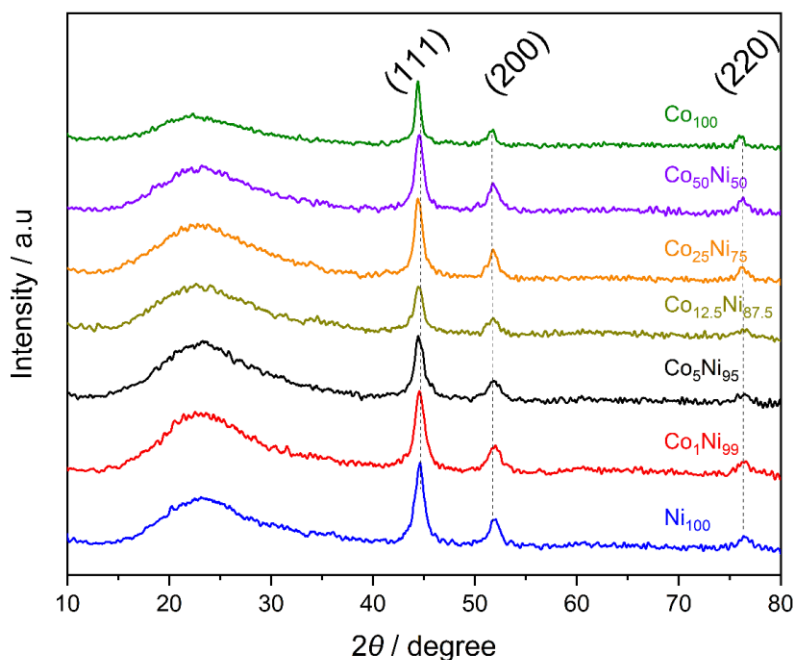


Figure 2.5 XRD patterns of $\text{Co}_x\text{Ni}_{100-x}@/\text{SiO}_2$ samples after reduction at 600 °C.

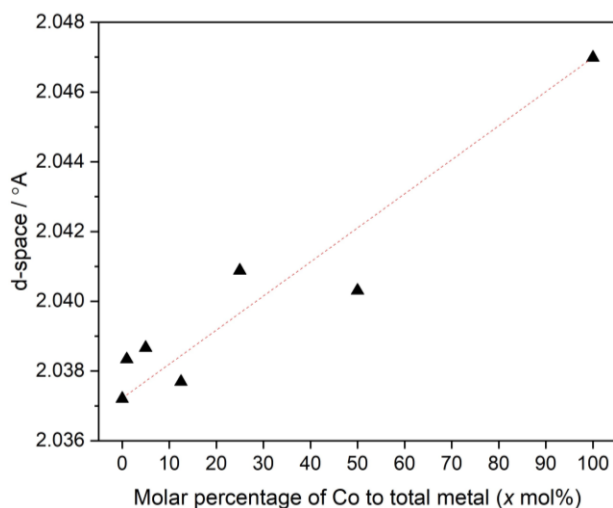


Figure 2.6 Lattice parameter (d-space, (111) plane) of Co–Ni alloy nanoparticles) in the $\text{Co}_x\text{Ni}_{100-x}@/\text{SiO}_2$ samples.

Based on the HAADF-STEM and EDX images (Figure 2.7), Co–Ni nanoparticles were encapsulated with SiO₂ yolk shell with a void space.

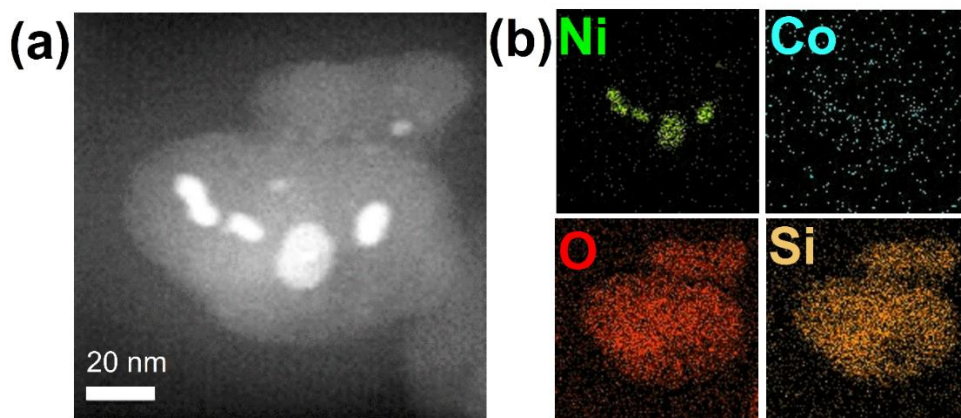


Figure 2.7 (a) HAADF-STEM and (b) EDX elemental mapping images of Co₅Ni₉₅@SiO₂ after reduction.

The compositions and physical properties are summarized in Table 2.1. The molar percentages of Co to the total metals (*i.e.*, the sum of Co and Ni) were almost identical to the used ones in the preparation. The total metal contents varied to some extent although we used constant time for the SiO₂ etching with hot water, presumably due to other factors such as surrounding temperature or holding time after the cooling process. The crystallite size of metal nanoparticles slightly decreased by the addition of tiny amounts of Co (1–5 mol %) from 8.3 to 7.8 nm. On the contrary, over 5 mol% Co, the crystallite size increased up to 10.5 nm in Co₅₀Ni₅₀@SiO₂ as the Co amount increased. The specific surface area of the samples showed a tendency to decrease with increasing Co content. The mean particle size by TEM followed a similar trend to the crystallite size of metal nanoparticles (Table 2.1) although the minimum value (3.6 nm) was obtained in a relatively larger Co amount of 12.5 mol%. The observed discrepancy in the crystallite size by XRD and particle size by TEM could be attributed to the particle size distribution,[22] which was partially supported by the numerical calculation of volume-weighted particle size from the TEM data.

Table 2.1 Characterization Results^[a]

Catalyst	Ni (wt%) ^[b]	Co (wt%) ^[b]	Co/M ^[c] (mol%)	d_{XRD} ^[d] / nm	d_{TEM} ^[e] / nm	S_a ^[f] / m ² g ⁻¹
Ni ₁₀₀ @SiO ₂	14.1	0	0	8.3	9.0	146
Co ₁ Ni ₉₉ @SiO ₂	20.5	0.2	1.0	7.8	7.6	78.2
Co ₅ Ni ₉₅ @SiO ₂	10.2	0.6	5.5	7.8	6.7	86.5
Co _{12.5} Ni _{87.5} @SiO ₂	12.4	1.8	13	9.4	3.6	89.8
Co ₂₅ Ni ₇₅ @SiO ₂	8.8	3.0	25	9.9	6.7	71.0
Co ₅₀ Ni ₅₀ @SiO ₂	5.6	6.5	54	10.5	8.3	24.8
Co ₁₀₀ @SiO ₂	0	15.7	100	15.9	22.3	29.0

[a] The data was obtained in the catalysts after reduction pretreatment at 600 °C for [d] and [e], and after calcination (i.e., before reduction) for [b] [c] and [f]. [b] Weight percentage of the metal estimated by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). [c] Atomic percentage of Co to the total metals (i.e., sum of Co and Ni) estimated by LA-ICP-MS. [d] Crystallite size of metal estimated by XRD. [e] Mean particle size of metal nanoparticles estimated by TEM. [f] Specific surface area obtained by BET method from N₂ adsorption isotherm.

Furthermore, the particle size distribution became narrower by the addition of 1–25 mol% Co as shown in Figure 2.8. The heterogeneous state of the metal oxides (*i.e.*, co-existence of NiO and Co₃O₄ phases) in the Co-rich samples (Co₂₅Ni₇₅@SiO₂ and Co₅₀Ni₅₀@SiO₂) after calcination (shown in Figure 2.3) is presumably responsible for the broad particle size distribution.

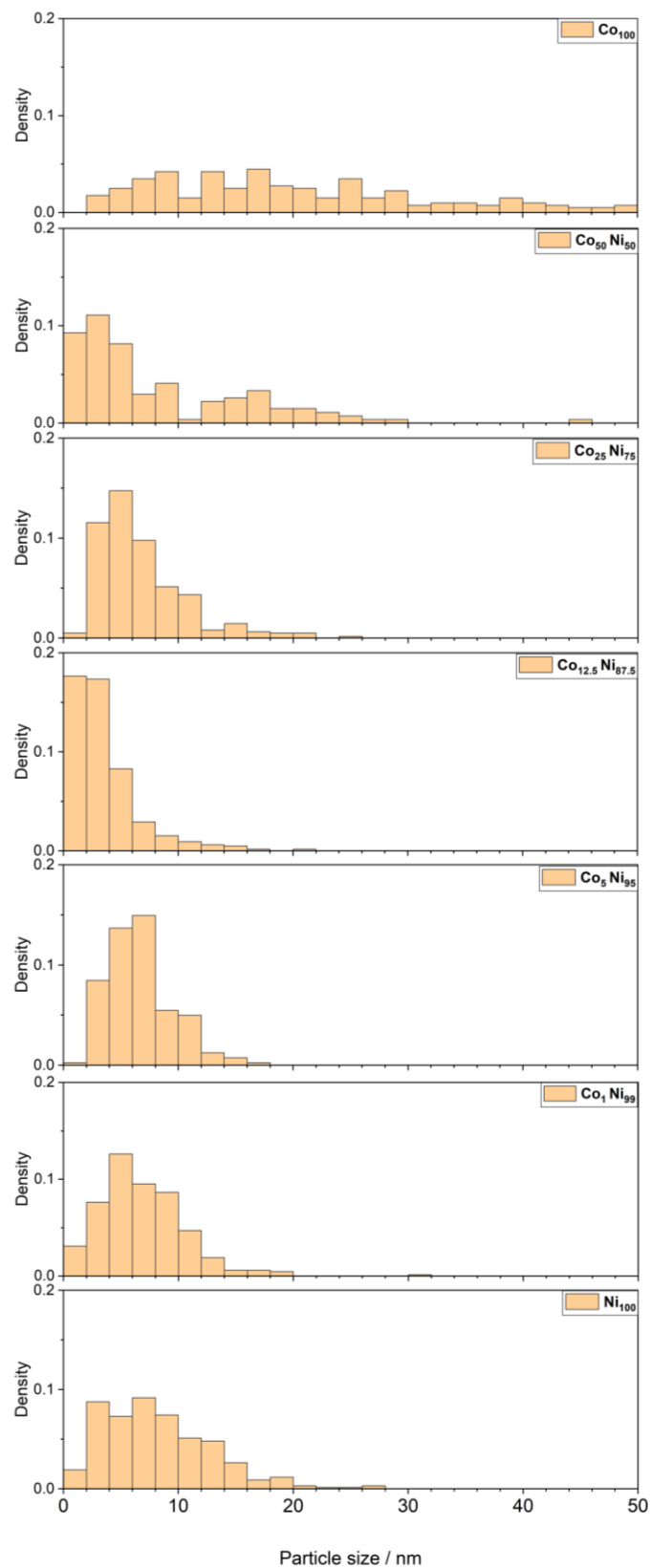


Figure 2.8 Particle size distributions of Co–Ni alloy nanoparticles in $\text{Co}_x\text{Ni}_{100-x}@\text{SiO}_2$ samples.

In the light absorption property, all $\text{Co}_x\text{Ni}_{100-x}@\text{SiO}_2$ catalysts showed low diffuse reflectance between 10–12% in 400–2000 nm region in UV–Vis–NIR DRS, indicating the fabricated materials absorb visible and near-IR light effectively in Figure 2.9. We compared the diffuse reflectance at 600 nm and the surface temperatures of the reactor under the photothermal reaction conditions (*i.e.*, shown in the Catalytic performance in PT-DRM section, Figure 2.11), as illustrated in Figure 2.10. The surface temperatures remained constant at approximately 540 °C across all samples. There was no clear correlation between diffuse reflectance and catalytic activity. Based on the results, we conclude that the light-induced temperature under irradiation is not the predominant factor for the photothermal catalytic performances in the present conditions.

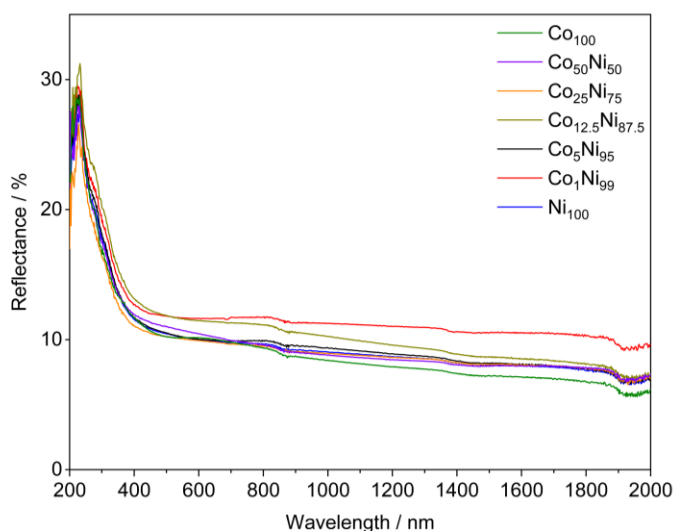


Figure 2.9 Diffuse reflectance spectra of the reduced $\text{Co}_x\text{Ni}_{100-x}@\text{SiO}_2$ catalysts.

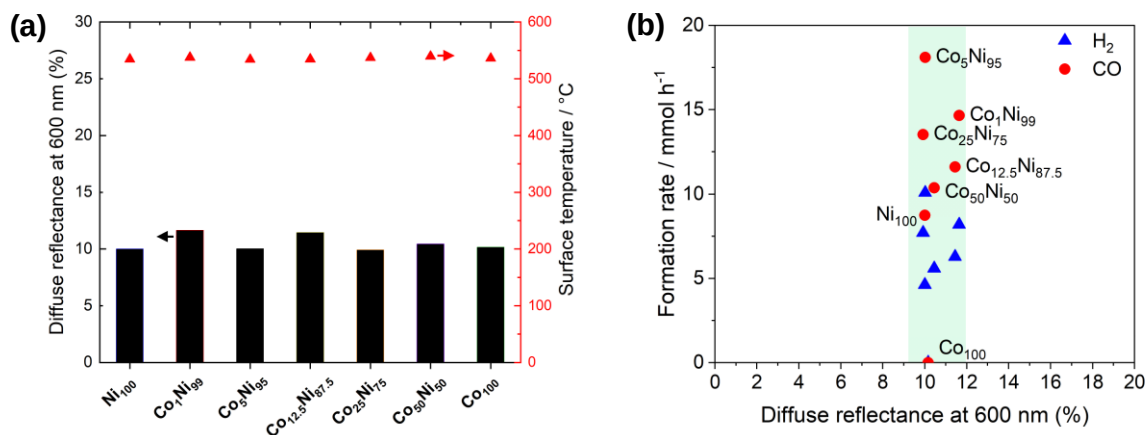


Figure 2.10 (a) Diffuse reflectance at 600 nm (left-axis) and the surface temperature of the reactor under photothermal reaction conditions in Figure 2.13 (right-axis), and (b) relationship between diffuse reflectance at 600 nm and CO and H_2 formation rates in $\text{Co}_x\text{Ni}_{100-x}@\text{SiO}_2$.

Catalytic Performance in PT-DRM

For the photothermal catalytic activity tests, we started the investigation with and without the etching treatment of the SiO₂ shell using hot water to fabricate the porous structure,[43] where the spot size and power of the light were set to be 19 mm and 18.2 W, respectively, as illustrated in Figure 2.1. Without the etching treatment, Ni₁₀₀@SiO₂ showed almost no activity in PT-DRM (Figure 2.11). A similar phenomenon was reported in thermo-catalytic DRM catalysts using an excessive SiO₂ shell.[38, 42, 46] In contrast, the etching treatment enhanced the activity significantly (45 times in CO formation). The specific surface area and pore volume (Figure 2.12) were significantly enhanced by the etching treatment based on the N₂ adsorption-desorption isotherms. Moreover, the BJH pore volume distribution plots showed an increase of mesopores less than 10 nm. These results indicate the etching treatment is effective in fabricating a porous SiO₂ shell that enables the reaction gases to diffuse to the active catalytic surface of the metal nanoparticles.

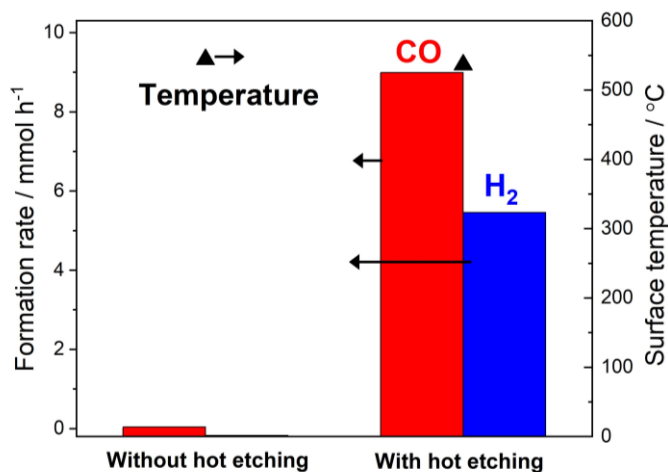


Figure 2.11 Results of activity test in PT-DRM on Ni₁₀₀@SiO₂ catalyst with and without hot etching treatment. The reaction time was 2 h. The activity tests were performed under the same conditions as Figure 2.13.

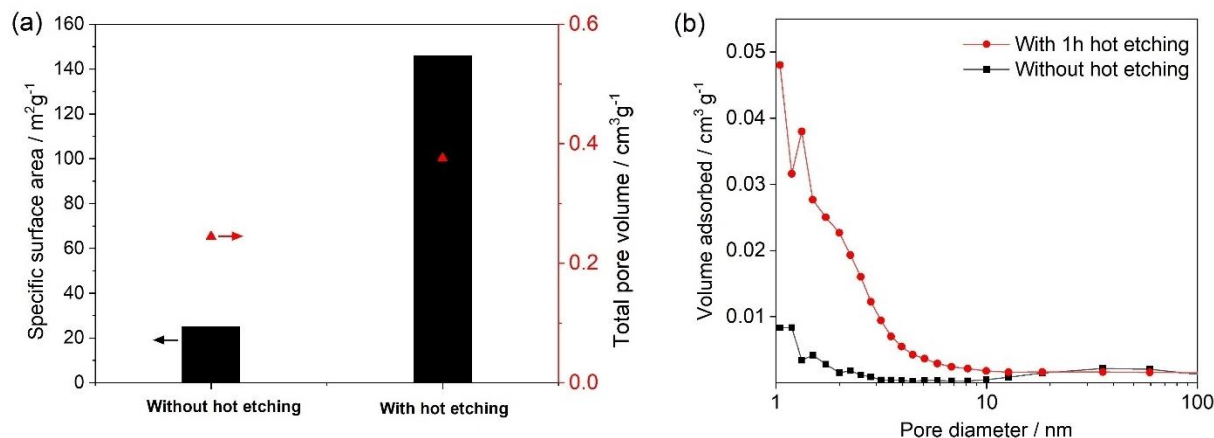


Figure 2.12 The specific surface area and pore volume (a), and corresponding BJH pore size distribution plots (b) for the Ni₁₀₀@SiO₂ samples with and without the hot etching treatment.

Then, we investigated the catalytic activity of the Co_xNi_{100-x}@SiO₂ catalysts after the etching treatment (Figures 2.13a and 2.13b). The above Ni₁₀₀@SiO₂ catalyst exhibited catalytic activity with high carbon balance of 98–99%; however, the formation rates of CO and H₂ decreased with a short reaction time of 2 h. In contrast, Co₅Ni₉₅@SiO₂ exhibited improved formation rates of CO and H₂ and enhanced stability compared to Ni₁₀₀@SiO₂. The further increase in Co amount decreased activity and stability. The Co₁₀₀@SiO₂ catalyst showed very low formation rates, consistent with observations in monometallic cobalt catalysts reported previously.[32, 33] Co₁Ni₉₉@SiO₂ and Co₅Ni₉₅@SiO₂ showed improved catalytic activity compared to the other catalysts although the total metal contents varied by around 10 wt%. This result suggests that metal composition has a dominant effect on the catalytic performance.

The highest surface temperature of the irradiated reactor, measured with the IR thermometer, reached around 538 °C in Co₅Ni₉₅@SiO₂ under light irradiation (Figure 2.13c). The surface temperature of the reactor tended to decrease as the measurement position departed away from the center of the reactor. There was no significant difference in the maximum temperature among the samples presumably due to their similar light absorption feature (Figure 2.9) and no correlation was observed between the diffuse reflectance and catalytic activity (Figure 2.10). The thermo-catalytic activity (*i.e.*, dark conditions) at 450 °C has a slightly different tendency in the activity and stability against the Co amount from the results of PT-DRM (Figure 2.14). Under concentrated visible/near-IR light, the photo-formed temperature gradients potentially change

catalytic activity[20] and selectivity,[21] implying that the difference in the activity between photothermal and thermo-catalytic systems is caused by the temperature distribution. We additionally investigated the catalytic performances in the thermo-catalytic system at 450–750 °C (Figure 2.15). The catalytic performances at the reaction temperature of 550 °C, close to the highest surface temperature under the irradiation conditions in Figure 2.13c, were approximately 2 times higher than those observed with the corresponding PT-DRM system (*i.e.*, Figures 2.13a and 2.13b). This suggests that the lower temperature zone surrounding the maximum temperature zone has a negative effect on the catalytic performance.

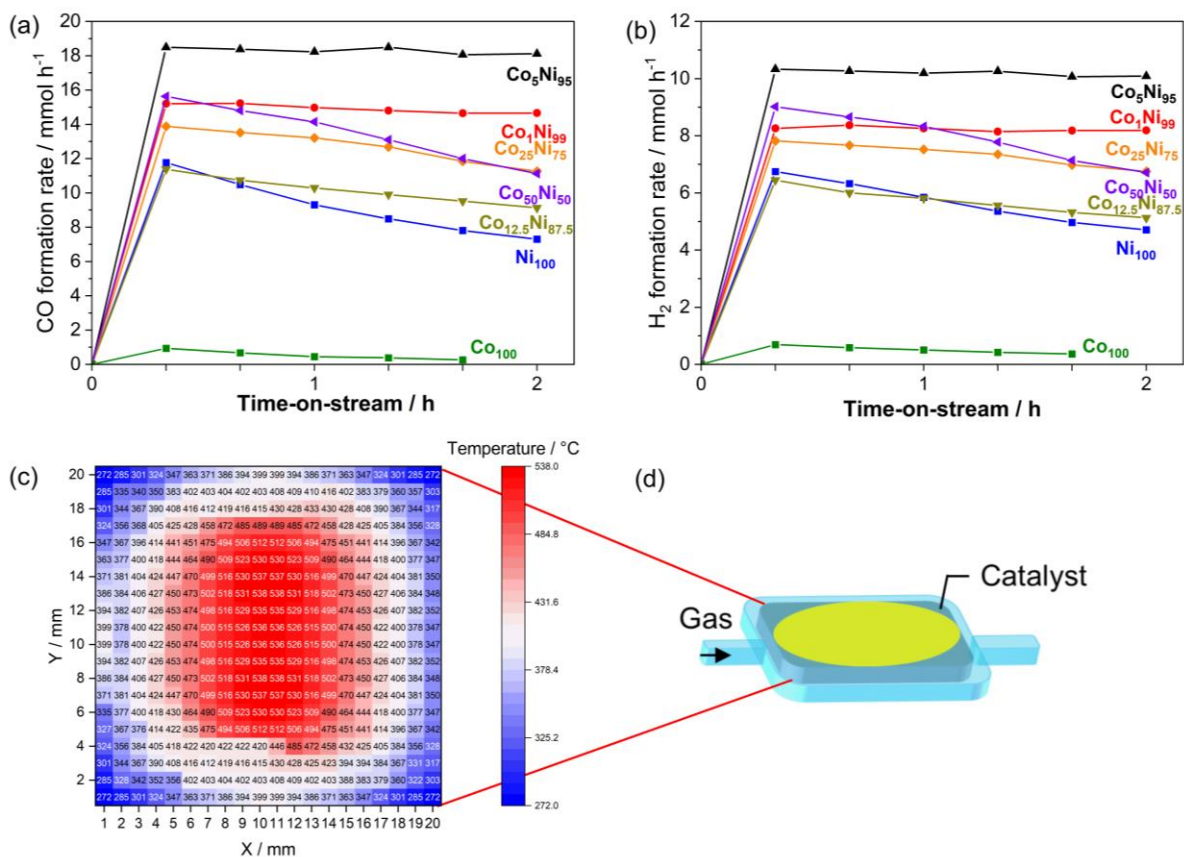


Figure 2.13 Time course of the formation rates of CO (h) and H₂ (i) in PT-DRM on Co_xNi_{100-x}@SiO₂. (c) 2D map of the surface temperature measured using IR sensor and (d) schematic representation of the reactor with the irradiated area (yellow).

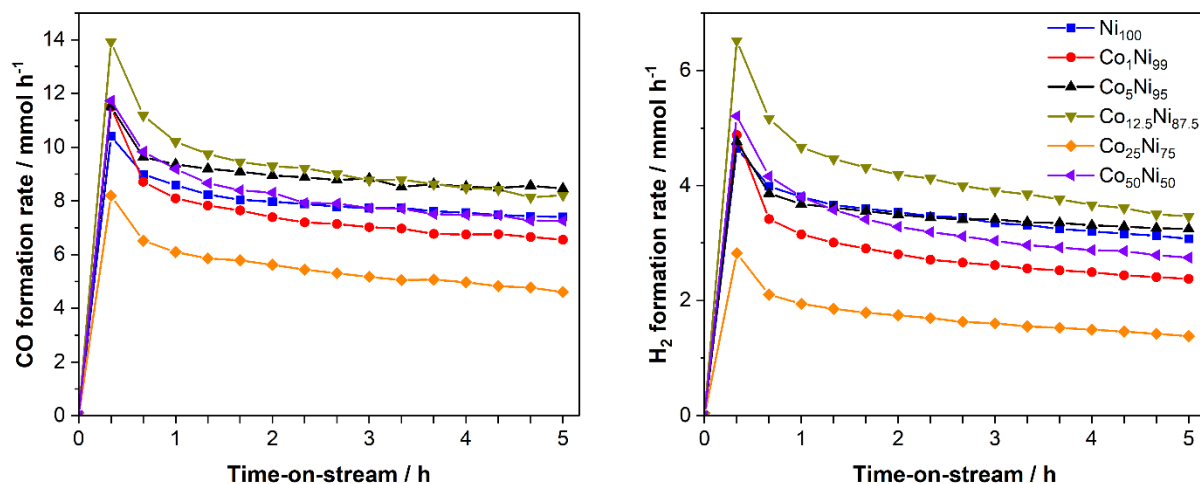


Figure 2.14 Formation rates of CO and H₂ in the thermal DRM reaction in dark at 450 °C. The catalyst amount: 50 mg, reactor: tubular reactor with an inner diameter of 4 mm. The other reaction conditions were the same as Figure 2.13.

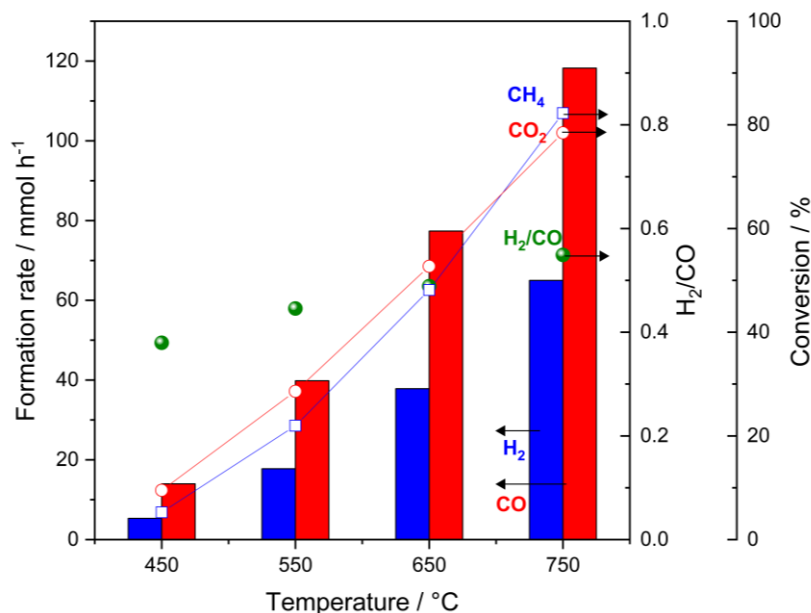


Figure 2.15 Temperature-dependent catalytic activity in thermal DRM on the Co₅Ni₉₅@SiO₂ catalyst in dark. The catalyst amount: 50 mg, reactor: tubular reactor with an inner diameter of 4 mm. The pretreatment and reaction conditions were the same as Figure 2.13.

Resistance for Coke Formation and Sintering

Coke formation and sintering of metal nanoparticles are the primary factors leading to deactivation in thermo-catalytic DRM.[35] The coke amount deposited after 2 h reaction (i.e., Figures 2.13) was quantified by elemental analysis and depicted in Figure 2.16. The addition of 1–5 mol% Co resulted in a substantial inhibition of coke formation. Moreover, H_2/CO ratio at 2 h exhibited a corresponding trend to the amount of deposited coke, where both were minimized with the addition of 5 mol% of Co. The morphology of carbon species by DRM typically varies such as amorphous coke, whisker coke, and graphitic coke[47–50]. In $Co_{50}Ni_{50}@SiO_2$, the whisker-shaped carbon species were formed by TEM after the 2-h PT-DRM reaction; contrary, no coke species were observed on the $Co_5Ni_{95}@SiO_2$ as shown in Figure 2.17.

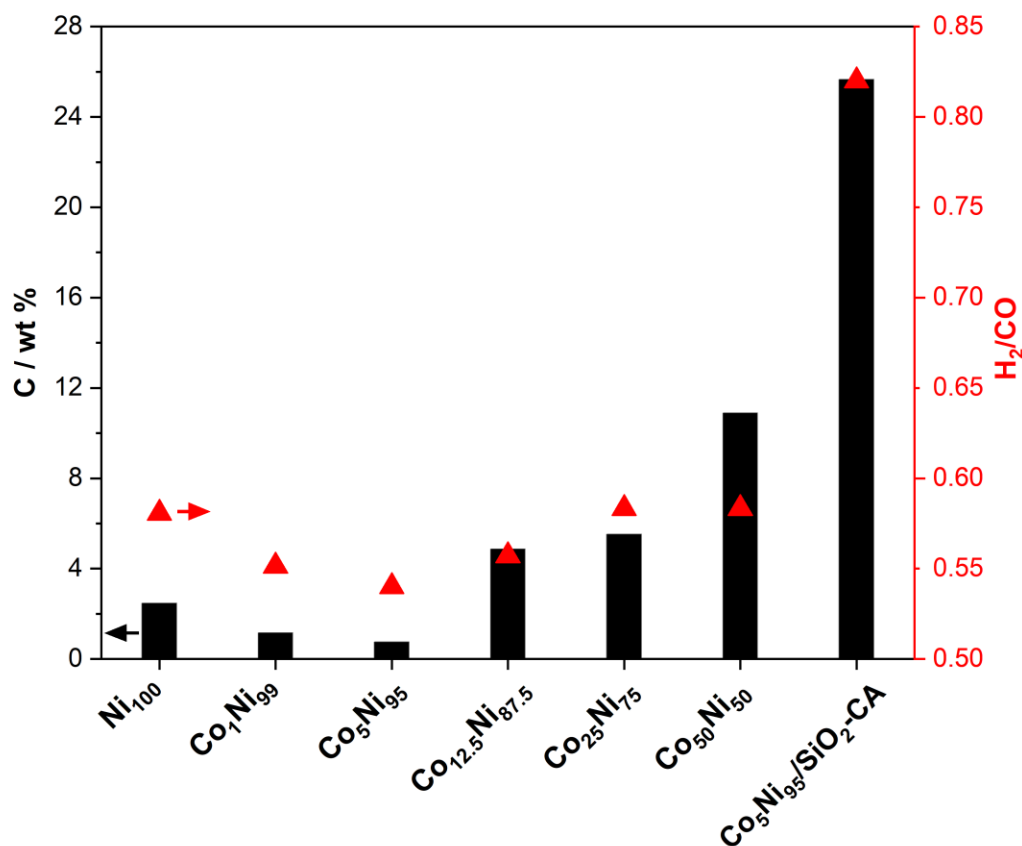


Figure 2.16 Amount of deposited coke and the H_2/CO ratio after the PT-DRM reaction. The reaction times in $Co_xNi_{100-x}@SiO_2$ and Co_5Ni_{95}/SiO_2-CA were 2 h and 40 min, respectively.

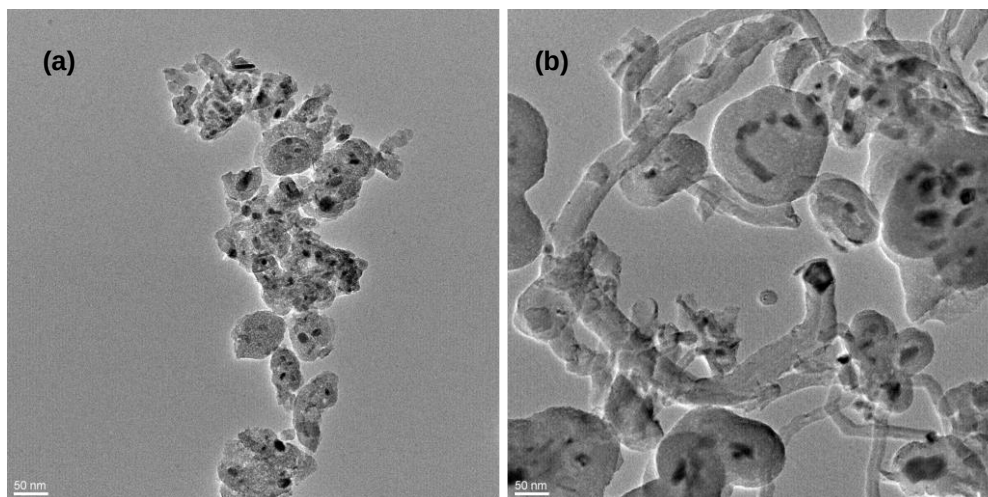


Figure 2.17 TEM images of the used catalysts after the 2-h PT-DRM reactions. (a): Co₅Ni₉₅@SiO₂ and (b): Co₅₀Ni₅₀@SiO₂.

In all samples, the H₂/CO ratio was lower than the stoichiometric value in DRM (eq. 2.1, *i.e.*, 1), as shown in Figure 2.16, possibly due to the concurrence of reverse water gas shift (eq. 2.6) and CO₂ methanation (eq. 2.7) reactions.[7][10]



It is well-known that CH₄ decomposition (eq. 2.8) and Boudouard (eq. 2.9) reactions are primary pathways for coke formation with increasing the H₂/CO ratio.[51]



The significant correlation observed between carbon deposition amount and H₂/CO ratio (Figure 2), which supports the coke formation occurred via these reactions in eqs. 2.8 and 2.9. In thermo-catalytic DRM, the addition of Co to Ni nanoparticles has been reported to enhance the activation of CO₂ to CO and surface oxygen (O_s) and the formed O_s promotes oxidation of surface CH_{*n*} (*n* = 0–3) intermediates for both of CO and carbon species.[33, 52–54] It is plausible that the presence of surface cobalt species promotes the oxidation of intermediate CH_{*n*} species to CO, effectively suppressing coke formation.

To evaluate the resistance against sintering, we measured the crystallite size of metal nanoparticles before and after the 2-h PT-DRM reaction by XRD. The crystallite size increased by 2.7 nm in $\text{Ni}_{100}@/\text{SiO}_2$ sample and by 0.9 nm in $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$ (Figure 2.18). These results indicate that the Co incorporation into the Ni nanoparticles suppresses the sintering, as reported in the thermo-catalytic DRM previously.[6, 55] Distinctively, severe sintering was observed by 5.2 nm in $\text{Co}_{50}\text{Ni}_{50}@/\text{SiO}_2$.

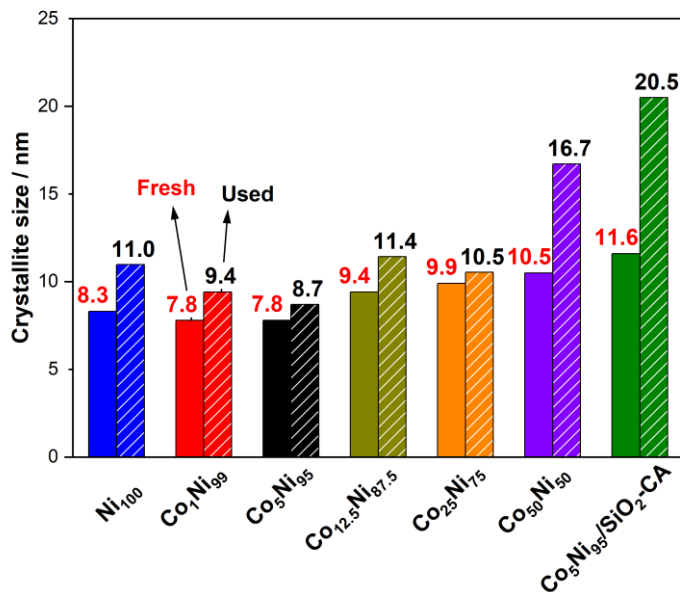


Figure 2.18 Crystallite size of Ni-Co alloy nanoparticles estimated by XRD. Fresh: the samples after the H_2 reduction pre-treatment at 600 °C, and used: the samples used after the PT-DRM reaction. The reaction times in $\text{Co}_x\text{Ni}_{100-x}@/\text{SiO}_2$ and $\text{Co}_5\text{Ni}_{95}/\text{SiO}_2\text{-CA}$ were 2 h and 40 min, respectively.

In the particle size distribution of $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$ by TEM (Figure 2.19a), slight sintering of metal nanoparticles was observed, while it was more obvious in $\text{Co}_{50}\text{Ni}_{50}@/\text{SiO}_2$ (Figure 2.19b). In both cases, the nanoparticles with a size of < 3 nm nearly disappeared after the 2-h PT-DRM reaction, possibly due to the low stability of the smaller nanoparticles.[22, 31] Such small nanoparticles would sinter under the reaction conditions, which results in the formation of larger nanoparticles (> 10 nm) that functions as coke formation sites.[31] In terms of the particle size, the homogenous particle size distribution with a moderate size (~7.8 nm) in $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$ likely contributes to the high stability due to fewer small particles (< ca. 3 nm) that cause sintering and few large particles (> ca. 10 nm) that are responsible for coke formation.

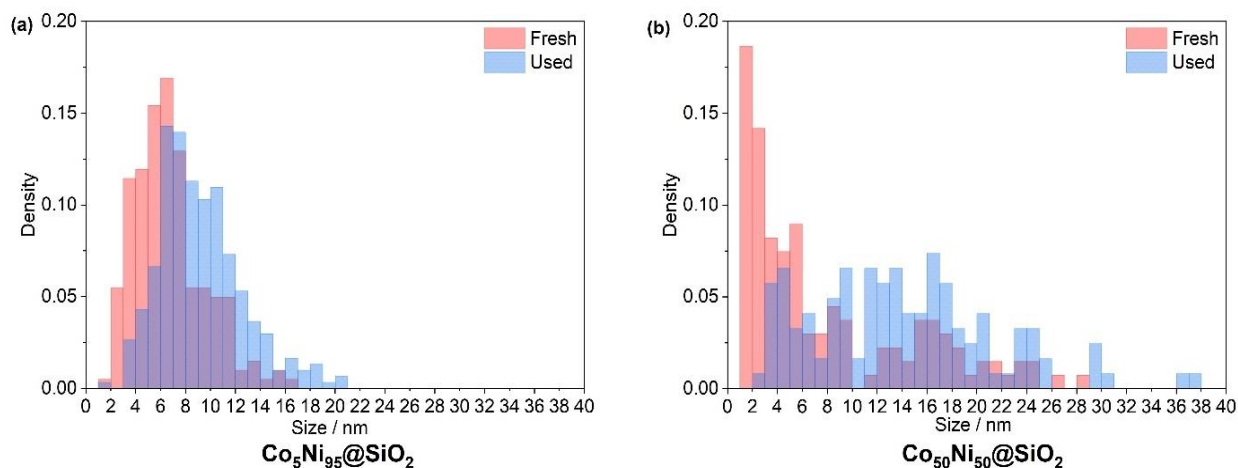


Figure 2.19 Particle size distribution for (a) $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$, and (b) $\text{Co}_{50}\text{Ni}_{50}@/\text{SiO}_2$ catalysts.

To assess the role of the SiO_2 shell on the stability, we performed activity tests using impregnation catalysts with the same compositions. The crystallite sizes of metal nanoparticles in the $\text{Co}_5\text{Ni}_{95}/\text{SiO}_2$ catalysts prepared by the conventional impregnation method with and without citric acid were 11.6 and 28.9 nm, respectively, estimated by XRD. Both catalysts showed significantly lower stability (Figure 2.20) than $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$. Even for the $\text{Co}_5\text{Ni}_{95}/\text{SiO}_2\text{-CA}$, having a comparable crystallite size to the $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$, severe coke formation was observed after the 40-min PT-DRM reaction (deposited coke amount: 25.6 wt%, Figure 2). Moreover, a rapid deactivation was similarly observed in the impregnation catalysts with the other composition of $\text{Co}_{12.5}\text{Ni}_{87.5}/\text{SiO}_2$ (Figure 2.20). The crystallite size increased by 9 nm in $\text{Co}_5\text{Ni}_{95}/\text{SiO}_2\text{-CA}$ after 40-min PT-DRM (Figure 2.18), which was significantly larger than that in $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$ (0.9 nm). These results indicate that the SiO_2 shell has a crucial role in suppressing both coke formation and sintering of the alloy metal nanoparticles.

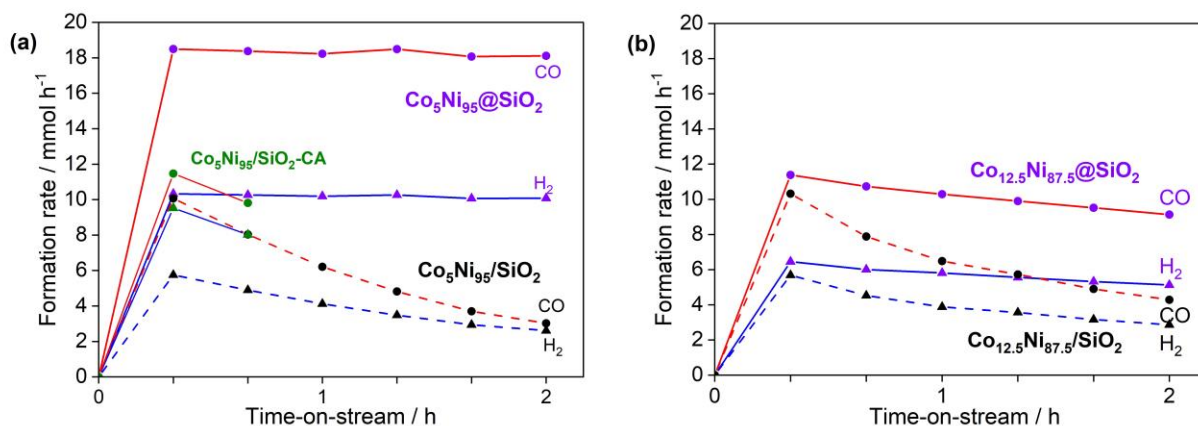


Figure 2.20 Catalytic activity comparison between Yolk-shell and Impregnation catalysts of (a) $\text{Co}_5\text{Ni}_{95}$ and (b) $\text{Co}_{12.5}\text{Ni}_{87.5}$.

The $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$ catalyst showed superior stability than monometallic Ni samples (i.e., $\text{Ni}_{100}@/\text{SiO}_2$) in the activity test of PT-DRM. The suppression of coke formation (Figure 2.16 and 2.17) and sintering (Figures 2.18 and 2.19) by the Co-Ni alloying likely contribute to the superior stability. In thermal DRM systems[32-34], the Co-Ni alloying is effective in suppressing coke formation, which suggests that this surface property also enhances the activity of PT-DRM. Note that neither SiO_2 encapsulation nor Co alloying alone was sufficient to suppress coke formation and sintering as shown in Figures 2.16 and 2.18. Thus, by combining the two strategies, we demonstrated that the stability was enhanced in the present conditions of PT-DRM with large temperature gradients.

Effect of Reaction Conditions

The reaction conditions were investigated using the $\text{Co}_5\text{Ni}_{95}@/\text{SiO}_2$ catalyst in PT-DRM. All activity tests were performed with a fresh catalyst at a reaction time of 0 h. As shown in Figure 2.21, increase of the light power elevated the surface temperature and photothermal catalytic activity. The highest CH_4 conversion (21 %) was obtained at a light power of 25 W (intensity: 8.8 W cm^{-2}).

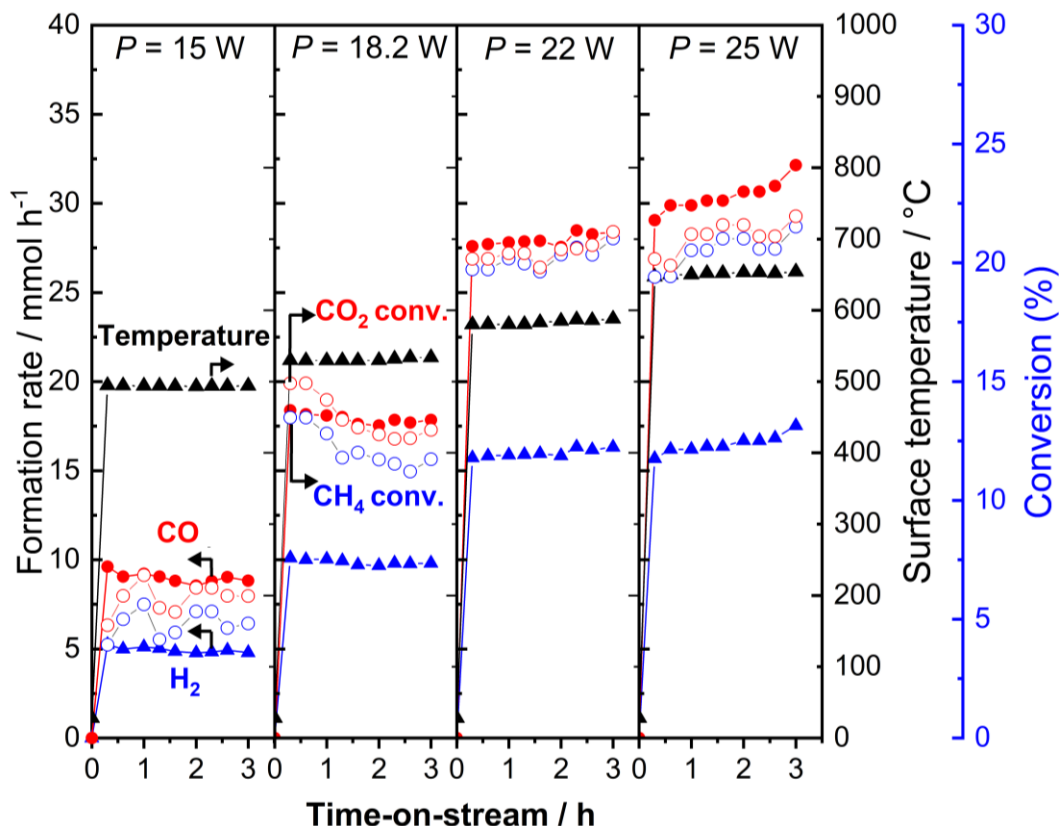


Figure 2.21 Effect of light power (P) on the photothermal catalytic activity (spot size: 19 mm, irradiation position: center).

Then, the light spot size (Φ) was changed at a fixed light power of 25 W as shown in Figure 2.22. As the spot size decreased from 19 mm to 7 mm (*i.e.*, increased light intensity at the spot), the surface temperature at the center of the spot increased systematically from 535 to 980 °C. In the spot sizes of 15 and 11 mm, the formation rates of CO and H₂ increased with the reaction time in the initial 3 h. In the subsequent changes after 3 h at $\Phi = 11$ mm, the activity peaked at 9 h (the maximum CO formation rate: 52 mmol h⁻¹), followed by a decline in the activity. The reasons for the time-dependent activity might be derived from the formed coke although they were not clarified at this stage. Throughout the investigation on the spot size, the CH₄ conversion did not change significantly with the rising surface temperature. In thermo-catalytic DRM, the activity typically increases with temperature.[56-58] With the data obtained in this study, we hypothesize that side reactions such as water-gas shift (the reverse reaction of eq. 2.6) or CO hydrogenation (eq. 2.10) occurred downstream of the highest temperature zone, as observed in Figure 1h, because

these reactions are preferable in the lower temperature range (< 500 °C) than that required for DRM (> 600 °C).[7, 35]

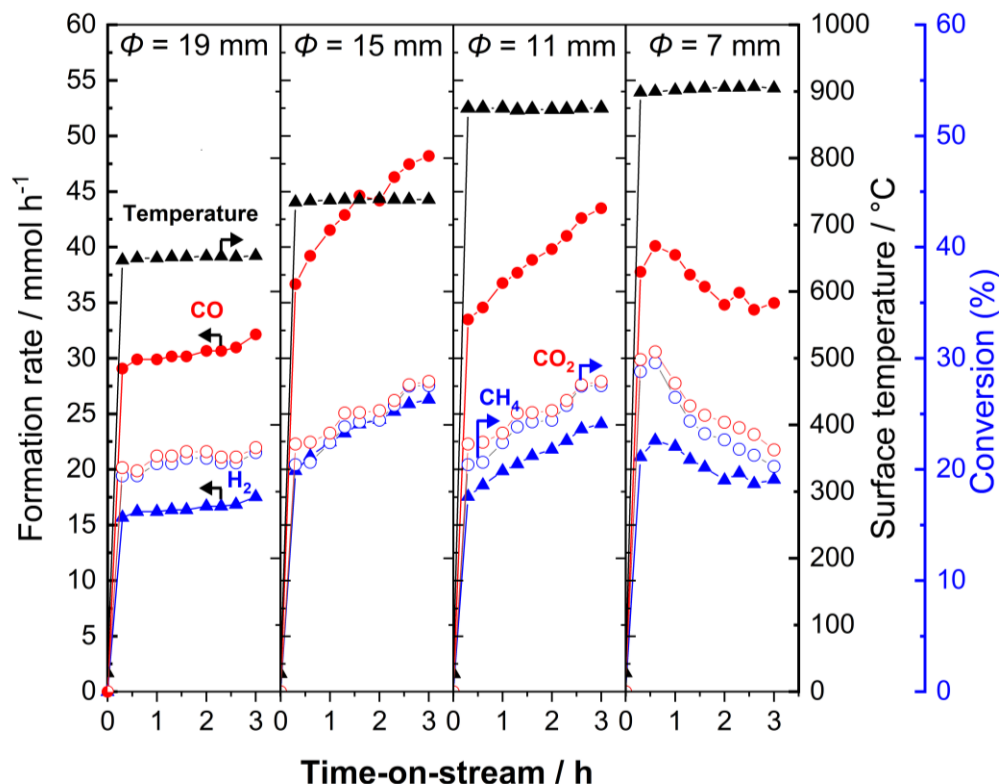


Figure 2.21 Effect of spot size (Φ) of concentrated visible-NIR light ($P = 25$ W, spot position: center).

To explore the contribution of such subsequent reactions in the downstream low-temperature zone, the catalytic performance was evaluated with various positions of the light spots. As shown in Figure 2.23, the upstream and middle zone irradiation showed no significant change, whereas CH_4 and CO_2 conversions were drastically enhanced to 40 % after 3 h by irradiating the downstream zone, likely due to the suppression of the reverse or side reactions. Furthermore, we investigated the PT-DRM reaction using the upstream irradiation by replacing the $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2$ catalyst in the downstream zone with silica granules (Figure 2.24). The conversion of CH_4 and CO_2 was improved from 25% (Figure 2.24, upstream) to 38% by replacing the downstream catalyst. These results indicate that the low-temperature zone of the downstream catalyst promoted the reverse reaction of PT-DRM in eq. 2.1.

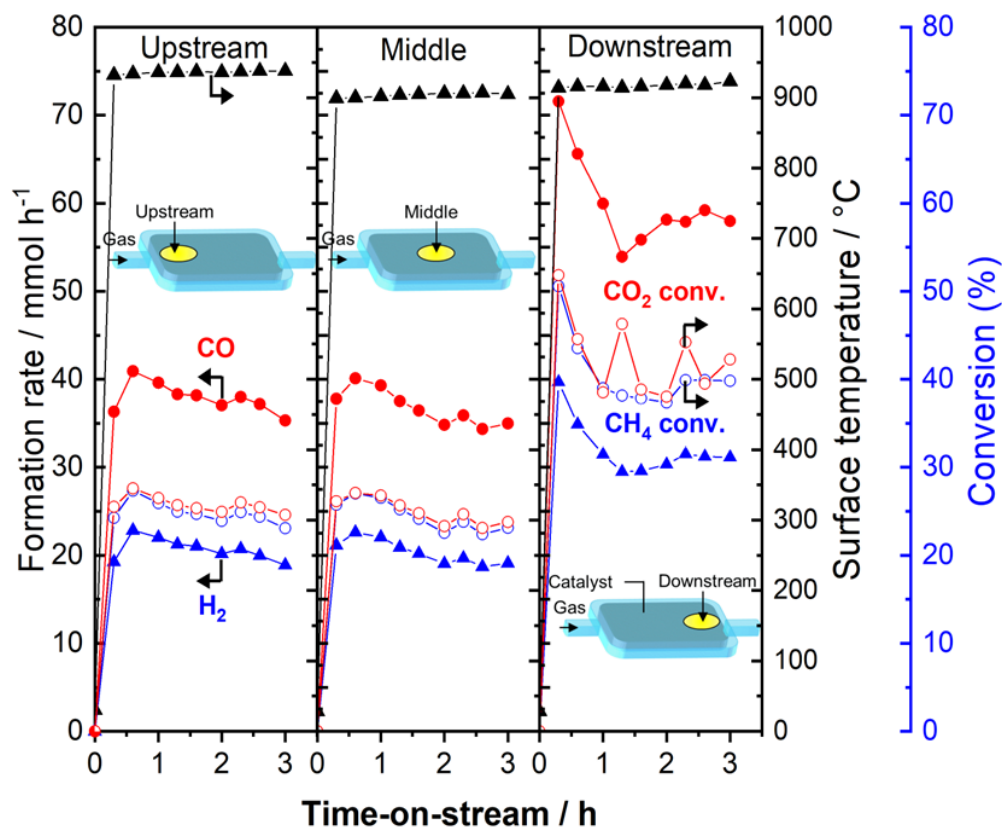


Figure 2.23 Effect of the spot position ($P = 25$ W, $\Phi = 7$ mm).

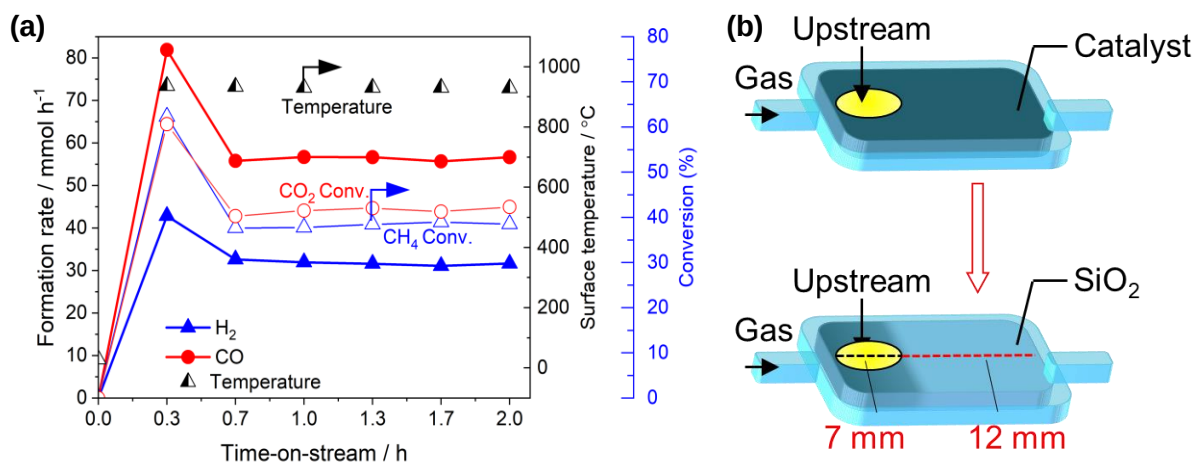


Figure 2.24 Time course of the formation rates of CO and H₂ (left axis) and the surface temperature (right axis) in PT-DRM on Co₅Ni₉₅@SiO₂ and SiO₂ (spot size diameter $\Phi = 7$ mm under light power = 25 W) and (b) the schematic illustration of the reactor and representation of the irradiated area.

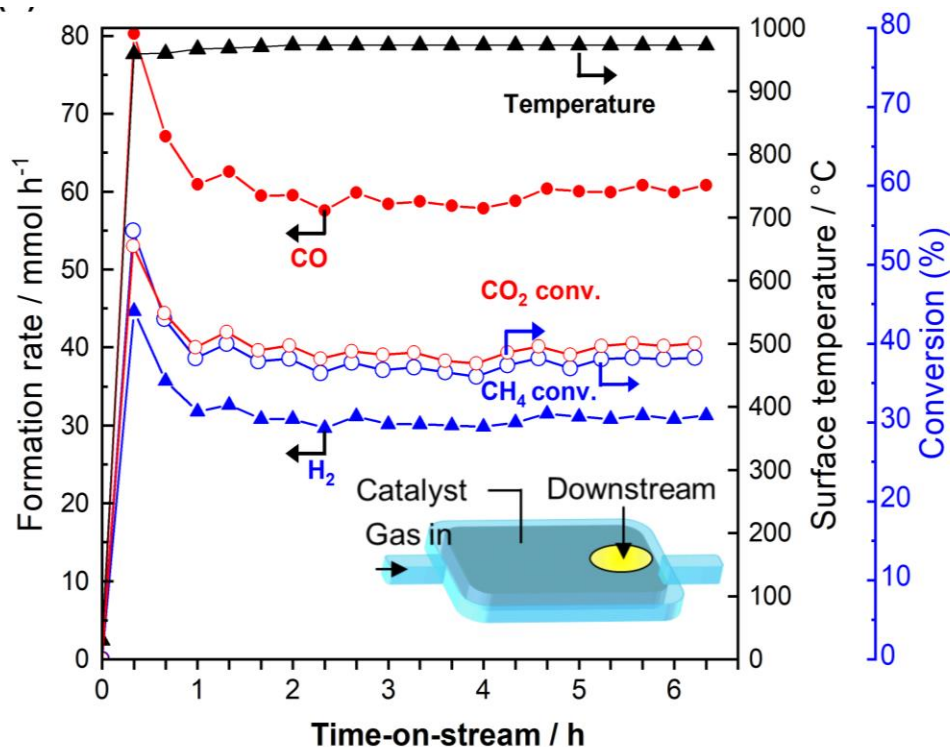


Figure 2.25 Long-time reaction of the $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2$ catalyst ($P = 25 \text{ W}$, $\Phi = 7 \text{ mm}$, position: downstream).

In the downstream irradiation, the initial activity decreased with time to some extent within 1 h, and subsequently, the CH_4 and CO_2 conversions remained steady at around 40 % for the next 5 h (Figure 2.25). The light-to-energy conversion efficiency calculated at the reaction time of 6 h was 6.5 % according to equation 2.5. The conversion level was moderate compared to the reported PT-DRM systems[9-19].-On the other hand, the light irradiation position was revealed to be a critical factor in improving the performance of PT-DRM, although it has rarely been studied in light-irradiated reaction systems.

Conclusion

In this study, we fabricated highly active and stable Co–Ni alloy nanoparticles encapsulated with a porous SiO₂ yolk shell for PT-DRM without additional external heating. Using Co alloying and SiO₂ shell encapsulation, the activity and stability were enhanced due to the improved resistance against coke formation and sintering of metal nanoparticles. Moreover, the investigation of irradiation conditions using the optimized Co₅Ni₉₅@SiO₂ catalyst revealed the irradiation parameters drastically affect the performance of PT-DRM. In particular, we revealed the photo-formed temperature gradient formed under light irradiation affected and limited the catalytic performance because of the reverse reaction at the low-temperature zone downstream. Moreover, we demonstrated that this limitation can be solved by simply changing the position of light irradiation. The insight obtained in this study presents the synthetic strategy to fabricate

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Chapter 3

Photothermal Tandem Catalysis of CH₄ Reforming and Fischer-Tropsch Synthesis to Produce Syngas and C₂₊ Hydrocarbons

Abstract

Photothermal catalysis is a promising approach for converting renewable solar energy to storable chemical energy. However, a critical challenge in photothermal catalysis lies in the temperature gradients formed under irradiation within the catalyst bed. In the present study, this temperature gradient is utilized to promote tandem reactions of the highly endothermic CH₄ reforming at the high-temperature zone to produce syngas and the exothermic Fischer-Tropsch synthesis (FTS) at the low-temperature zone to yield C₂₊ hydrocarbons. This study demonstrates that C₂₊ hydrocarbons such as ethane and ethylene are formed using a single photoreactor with a temperature gradient from CO₂ and CH₄ as carbon sources via the tandem reactions over SiO₂-encapsulated Co–Ni alloy catalysts. Almost no C₂₊ formation under uniform temperature conditions in an electric furnace highlights the essential role of the temperature gradient in C₂₊ formation. Moreover, this study reveals that the fabrication of the porous SiO₂ shell and the addition of steam into the feed gas have a crucial impact on the C₂₊ formation rate. This work may open new avenues for tandem reaction systems from two greenhouse gases of CO₂ and CH₄ into value-added C₂₊ hydrocarbons.

Introduction

Dry reforming of methane (DRM, eq. 1) is an appealing catalytic pathway that contributes to reducing CO₂ and CH₄ emissions and recycling them into syngas, a vital chemical feedstock.[1-5] On the other hand, several issues have been recognized: the low H₂/CO ratio (< 1) in the produced syngas for the post catalytic processes such as Fischer-Tropsch synthesis (FTS) or methanol synthesis and the low catalyst stability due to coke deposition and sintering.[1, 6-8] Combining steam reforming (SRM, eq. 2) with DRM is effective in increasing the H₂/CO ratio to suit the optimum ratio of syngas for FTS between 1–2 in a process known as bi-reforming of methane (BRM).[9, 10] In addition, the coke deposition can be mitigated in the presence of steam. [9, 10]



These CH₄ reforming reactions, however, are highly endothermic and require considerably high temperatures to achieve sufficient CH₄ conversion level. [1-4] Solar energy was proposed to energize these reactions through photothermal catalysis. [11-14] The advantage of the photothermal catalysis relies in its potential to replace the fossil-fuels in driving the CH₄ reforming reaction and decrease the carbon footprint. [13-15] Recently, photothermal reactions have received considerable attention and were applied in SRM [16, 17], DRM [1, 18-22], FTS [23, 24], and CO₂ hydrogenation [25-29]. Although huge efforts have been devoted to improving the photothermal catalytic reactions, there are few reports on photothermal BRM. [30, 31]

In the practical utilization of concentrated solar light, the non-uniform distribution of photon flux and the limited effective depths of catalyst for light absorption inevitably form a temperature gradient in the catalyst bed. [32, 33] This temperature gradient has frequently been considered a huge setback in the photothermal catalysis because it promotes the reverse reaction or undesired side reactions in the low-temperature zone. [16, 22]

In the present study, we utilized this temperature gradient in promoting multiple reactions to develop one-pass tandem catalytic reaction. This tandem process combines CH₄ reforming (eq. 1-2) and FTS (eq. 3-4) in one reactor to obtain value-added lower alkane or alkene

(C₂₊). Typically, CH₄ reforming reactions operate at high temperatures > 600 °C, while the suitable temperature range for FTS is 200–350 °C. The large difference in these reaction temperatures prevents the occurrence of both reactions in one reactor with a uniform temperature. The tandem process using a photothermally-induced temperature gradient can promote both reactions by utilizing the suitable temperature zone for each of these reactions.



In the catalyst materials, several active metal components (Fe, Co, Ni, and Ru, etc.) have been reported to catalyze both CH₄ reforming [1-5] and FTS reactions [34-40]. Very recently, we reported the Co–Ni alloy nanoparticles encapsulated with porous SiO₂ yolk-shell (Co–Ni@SiO₂) was effective for the photothermal DRM reaction with high resistance to coke deposition and sintering.[22] Herein, we report the successful formation of C₂₊ hydrocarbons by utilizing the photothermally-induced temperature gradient on the Co–Ni@SiO₂ catalysts. The temperature gradient enabled the tandem reactions of the endothermic CH₄ reforming reaction to proceed at the high-temperature zone and the exothermic FTS reaction at the downstream low-temperature zone.

Experimental

Catalyst Synthesis

Co–Ni alloy nanoparticles encapsulated with SiO₂ shell catalysts were prepared according to our previous report [22] with slight modification as illustrated in Figure 3.1. First, hydroxides of Co and Ni were synthesized by hydrothermal method. The total metal amount was 6 mmol of metal nitrate precursors were added to a solution of polyvinylpyrrolidone (PVP, 3 g) dissolved in deionized water, DIW, 120 mL) under Ar flow. After the dropwise addition of a NaOH solution (30 mL, 1 M) to the above solution, the mixtures were hydrothermally treated for 6 h at 150 °C using a Teflon-lined autoclave. After cooling to room temperature, the slurry obtained was washed 3 times with DIW by decantation.

The prepared nanoplatelets were encapsulated with various amounts of SiO₂. The suspension of each hydroxide was dispersed in DIW (total volume: 150 mL), followed by the addition of ethanol (300 mL) and aqueous NH₃ solution (28%, 15 mL) sequentially. Separately,

the designated amount of cetyltrimethylammonium bromide (CTAB) was dissolved in ethanol/DIW (50 vol%, 40 mL) (Table 3.1, shown in section 3.1). Then, designated amounts of tetraethyl orthosilicate (TEOS) and the CTAB solution were simultaneously added to the suspension of hydroxide dropwise. After 1 h of vigorous stirring, stirrer was stopped and the suspension settled down. The supernatant (250 mL) was decanted, the remaining suspension (200 mL) was dried at 80 °C in water bath to evaporate the solvent, followed by drying in oven overnight. The samples were calcined at 500 °C for 1 h or 550 °C for 6 h at the heating rate of 10 °C min⁻¹. The other monometallic or bimetallic catalysts containing Cu and/or Fe were also prepared using the same method except for the metal precursors (i.e., copper nitrates and iron nitrates). In the synthesis of Ru hydroxide, 3.4 mmol of RuCl₃·xH₂O (x = 1–3) aqueous solution was used as precursor. The samples were denoted as M(I)@SiO₂(y) or M(I)_xM(II)_{100-x}@SiO₂(y), where the M(I) and M(II) are the metal elements used, x is the content of M(I) to the total metal(s), and y is the calcination temperature.

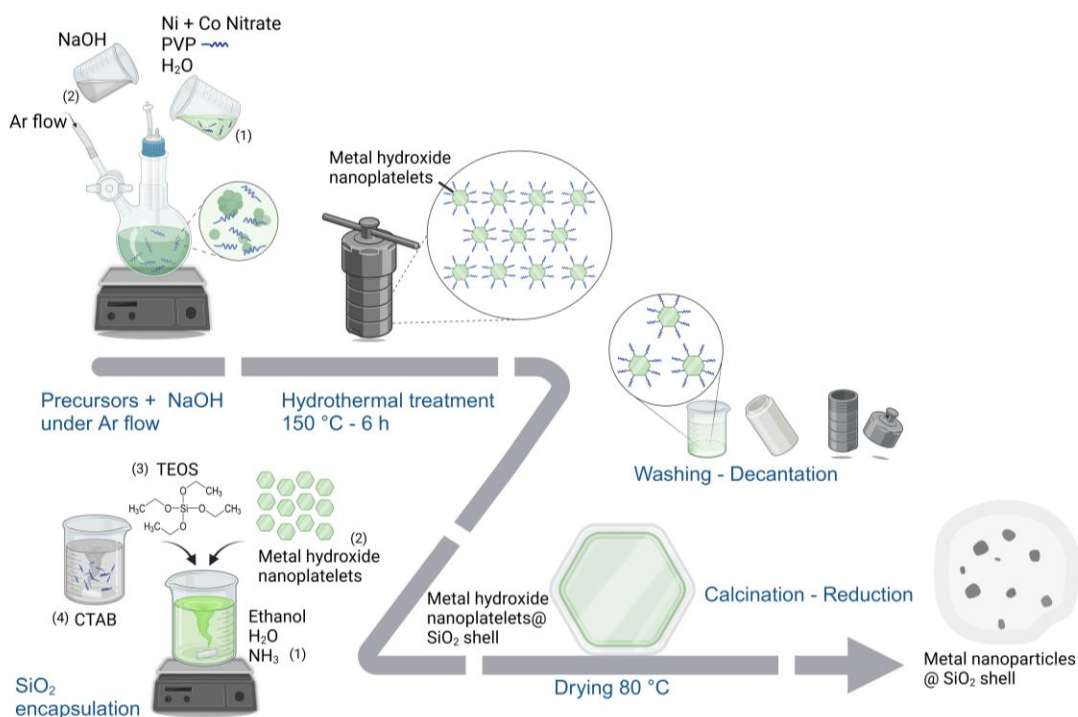


Figure 3.1. Schematic representation of the preparation procedure of the yolk-shell catalysts.

Impregnated catalysts were prepared using the wet impregnation method to evaluate the activity and product distribution. To prepare 10 wt% Co/SiO₂, cobalt nitrate precursor was dissolved in 25 mL DIW and was added to the suspension (100 mL) of commercial SiO₂ (Sciqas) followed by stirring for 30 minutes. Then the solvent was driven off on hotplate stirrer set at 80 °C, then transferred to an oven for aging at the same temperature overnight. The dry samples were then calcined at 450 °C for 2 h (10 °C/min).

Characterization

The metal contents of calcined samples were determined using an inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8900, Agilent Technologies Inc., Hachioji, Japan) connected to a femtosecond laser system with a galvanometric scanner (Raijin α , Seishin Trading Co., Ltd., Kobe, Japan). The weight of Si, Ni, Co, and Ru were calibrated using NIST SRM 610 [41]. Small amounts of oxygen (0.45 mL/min) gas were introduced into a collision/reaction cell between quadrupole mass filters to extend dynamic ranges. The $^{59}\text{Co}^+$ and $^{60}\text{Ni}^+$ were monitored for the NIST SRM 610, whereas the $^{59}\text{Co}^{18}\text{O}^+$ and $^{60}\text{Ni}^{18}\text{O}^+$ were monitored for the calcined samples. By determining production rates of the oxide ions, calibration of signal intensities between the atomic and oxide ions can be made. X-ray powder diffraction (XRD) patterns were recorded on a LabX XRD-6000 (Shimadzu, Japan) with Cu K α radiation, and the crystallite size of the metal was calculated from the diffraction peaks. Hydrogen temperature-programmed reduction (H₂-TPR) was investigated using a home-made setup featuring a quartz tube cell and BELMASS mass spectrometer (MicrotracBEL, Japan) under a flow of 10% H₂/Ar gas at 30 mL min⁻¹. Nitrogen adsorption-desorption isotherms were obtained using the BEL-MAX-G instrument (MicrotracBEL, Japan), and the porosity of the catalysts was assessed via the Barrett–Joyner–Halenda (BJH) method. UV-visible-near-IR diffuse reflectance spectra (UV-Vis-NIR DRS) were collected using a V-570 spectrophotometer (JASCO, Japan) with a BaSO₄ plate as the baseline reference. Transmission electron microscopy (TEM) analysis was carried out on a JEM-2200FS instrument (JEOL, Japan). Two gas chromatographs (GC) were used for online analysis of the effluent gases. A Shimadzu GC-8A equipped with a thermal conductivity detector (TCD) was used to quantify the primary gases (H₂, N₂, CO, CH₄, and CO₂) using a Shincarbon ST column. A Shimadzu GC-2014 equipped with a micro-packed Shincarbon ST column and a flame-

ionization detector were used for separating and quantifying gaseous hydrocarbons with 1-5 carbon atoms.

Catalytic Activity Tests

Photothermal and thermal activity tests were conducted using a fixed-bed continuous-flow system under ambient pressure. Catalyst powder was first pelletized at 40 MPa, then crushed and sieved to obtain granules with diameters between 150–300 μm . 0.3 g of granules were placed in a flat quartz reactor [22] (20 mm $\times$ 20 mm $\times$ 1 mm). In case of the dual-bed layout, 0.14 g of one catalyst, then 2-mm separator of quartz sand (40 mg) followed by 0.14 g of another catalyst were used (Figure 3.2). Prior to the activity test, the catalyst was treated by heating to 450 $^{\circ}\text{C}$ under an Ar flow, followed by oxidation for 30 minutes in an O_2 gas flow (100%, 5 mL min^{-1}) to remove any organics. Then, the catalyst was reduced for 30 minutes using 10% H_2/Ar gas (100 mL min^{-1}) at 600 $^{\circ}\text{C}$. After cooling under an Ar flow, reactants gas mixture ($\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2/\text{Ar}$ were 2/1/1/1/5 (Ar: 50 mL min^{-1}) was introduced into the reactor. To introduce the H_2O vapor, temperature-controlled H_2O trap was used prior to the reactor. For the photothermal reaction test, a 300 W Xe lamp equipped with a 435 nm cut-off filter and a focusing lens was used for light irradiation. The irradiated light power was measured using a thermal power sensor (S425C-L, Thorlabs Inc., USA). The power (P) and the inner diameter of the irradiated spot (Φ) were adjusted by varying the current of the power supply and the distance between the light source and the reactor, respectively. For thermal activity tests without light irradiation, catalyst granules (50 mg) were placed in a quartz tube reactor (inner diameter: 4 mm) and heated using a tubular electric furnace.

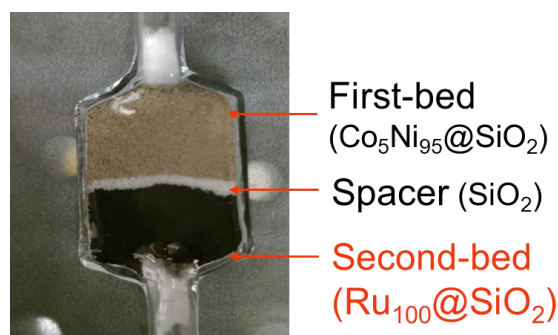


Figure 3.2 Photograph featuring the quartz reactor filled with $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(550)$ and $\text{Ru}_{100}@\text{SiO}_2(550)$ separated by quartz sand before the PT-BRM activity test. The color of $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(550)$ was brown before reduction pretreatment.

The formation rates of C₂₊ products (r_i , i = each C₂₊ product) was obtained from the peak area of the gas chromatograph and the calibration factors. Selectivity to molecule i were calculated from equations 3.6:

$$S_i = \frac{r_i}{r(total)} \times 100 \quad (3.6)$$

where $r(total)$ is the sum of r_i .

Results and Discussion

The Effect of Metal Loading

First, we optimized the total metal content in the catalysts using the Co₅Ni₉₅@SiO₂(500) in 7.5, 10, and 15 wt%. In all metal content, the Co–Ni oxide nanoparticles encapsulated with SiO₂ shell were obtained after the calcination at 500 °C based on XRD (Figure 3.3). The crystallite sizes of metal oxide nanoparticles were 3.7–4.3 nm (Table 3.1). The N₂ adsorption-desorption isotherms (Figure 3.4a) of the three samples showed characteristic shape of the type IV isotherms with H3 hysteresis loop, which suggests the presence of combination of micropores (less than 2 nm) and small mesopores. With increasing the metal loading from 7.5 to 15 wt%, the specific surface areas decreased from 157 to 95 m² g⁻¹ (Table 3.1 and Figure 3.4).

Table 3.1 Catalysts with different metal loading

Catalyst	TEOS / mL	CTAB / g	Crystallite size by XRD / nm	$S_a^{[c]}$ / m ² g ⁻¹	Pore volume $V_p^{[d]}$ / cm ³ g ⁻¹	Average pore diameter $d_p^{[e]}$ / nm
7.5 % Co ₅ Ni ₉₅ @SiO ₂	15.54	2.70	3.7	157.4	0.39	9
10 % Co ₅ Ni ₉₅ @SiO ₂	11.75	2.02	4.7	152.8	0.41	8
15 % Co ₅ Ni ₉₅ @SiO ₂	7.27	1.27	4.3	95.9	0.59	25

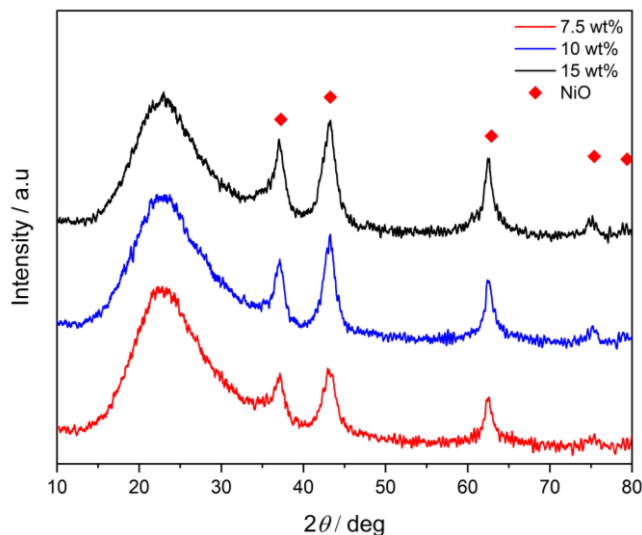


Figure 3.3 XRD patterns of the $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(500)$ catalyst with 7.5–15 wt% metal loading

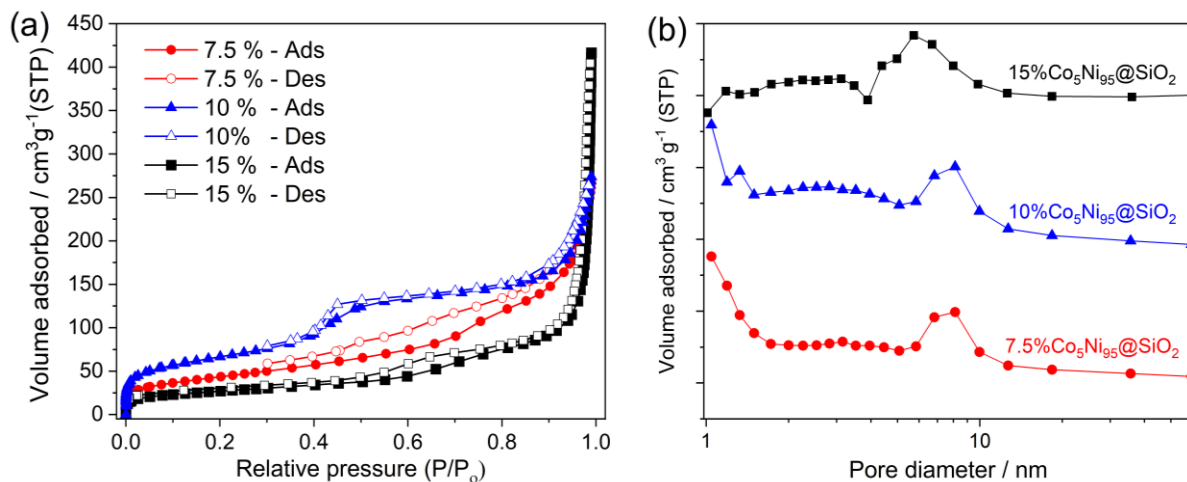


Figure 3.4 (a) Adsorption-desorption isotherm and (b) pore size distribution of the different metal loadings wt% calculated by BJH method of the calcined 7.5–15 wt% $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2$ catalysts at 500 C for 1 h.

For the initial stage of the PT0.-BRM activity tests, we irradiated the top position of the reactor with spot size of 7 mm as shown in Figure 3.5. The 7.5 wt% $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(500)$ catalyst showed the highest catalytic activity for syngas in the PT-BRM reaction with CO and H_2 formation rates of 1 h were 32 and 36 mmol h^{-1} , respectively (CH_4 conversion: 30%, CO_2 conversion: 45%) among the three samples. The initial activity was maintained for 1.3 h, and the highest temperature of the reactor surface reached around 1013 $^{\circ}\text{C}$. Surprisingly, we observed simultaneous formation of paraffins and olefins of C_{2+} with syngas in these activity tests. The highest formation rates of C_{2+} were also obtained on 7.5 wt% $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(500)$ catalyst (17.5 $\mu\text{mol h}^{-1}$), followed by the 10 wt% (7.9 $\mu\text{mol h}^{-1}$) and 15 wt% (2.7 $\mu\text{mol h}^{-1}$) catalysts as shown in Figure 3.6. The performance for C_{2+} formation correlated to the syngas formation rate, which suggests that the formed syngas is converted to C_{2+} hydrocarbons probably via FTS reaction pathway.

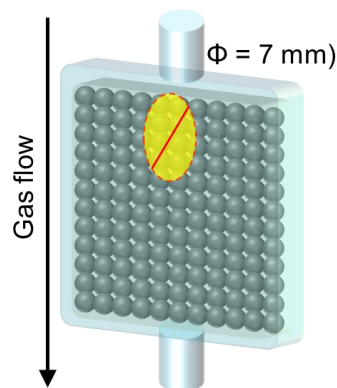


Figure 3.5 The schematic representation of the Top position irradiation with irradiated spot $\Phi = 7$ mm

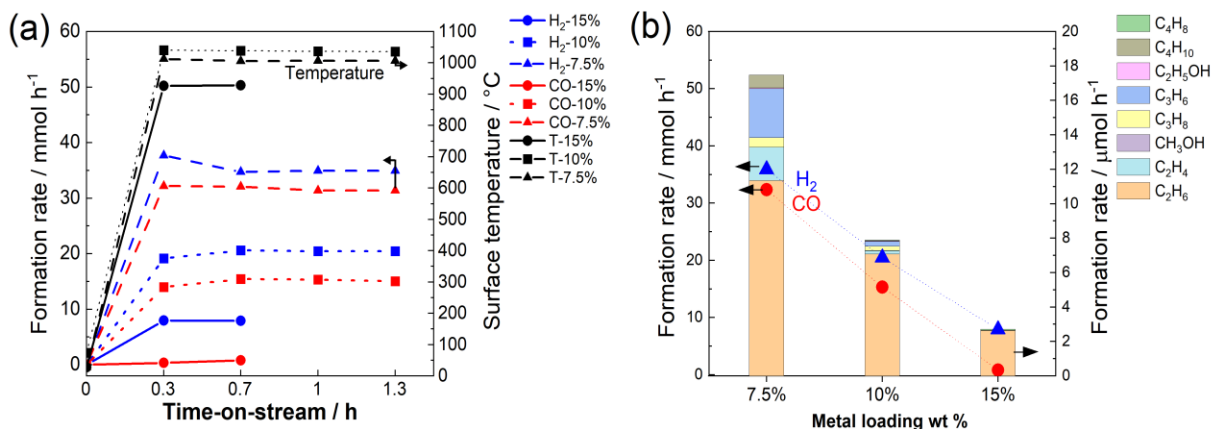


Figure 3.6 (a) H_2 and CO formation rates, and (b) C_{2+} hydrocarbons using 7.5, 10, and 15 wt% $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(500)$ catalysts ($P = 25.0$ W, $\Phi = 7$ mm, spot position: Top, $F = 100$ mL min^{-1}).

Effect of Reaction Conditions

To improve the performance of the C_{2+} formation, we investigated effect of reaction conditions on C_{2+} formation rates using the 7.5 wt% $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(500)$ catalyst. We first

examined the effect of the oxidant using mixture of CO₂ and H₂O (PT-BRM) or CO₂ alone (PT-DRM) on the formation rates of syngas and C₂₊ (Figure 3.7). In the conditions of the same the oxidant/CH₄ ratio, was maintained at unity, the total syngas formation rates ($\dot{r}_{syn} = \dot{r}_{CO} + \dot{r}_{H_2}$) did not change significantly in both PT-DRM ($\dot{r}_{syn} = 73 \text{ mmol h}^{-1}$) and PT-BRM ($\dot{r}_{syn} = 68 \text{ mmol h}^{-1}$) reactions. In contrast, the H₂/CO ratio increased from 0.56 in PT-DRM to around 0.90 in PT-BRM. Production rates of C₂₊ hydrocarbons in PT-BRM ($17.5 \text{ } \mu\text{mol h}^{-1}$) was over two times than that in PT-DRM ($7.6 \text{ } \mu\text{mol h}^{-1}$). The higher formation rates of C₂₊ hydrocarbons in PT-BRM could be ascribed to either the positive impact of the higher H₂/CO ratio on the successive FTS reaction [53, 54] or the contribution of the adsorbed water species to the C₂₊ formation [55, 56].

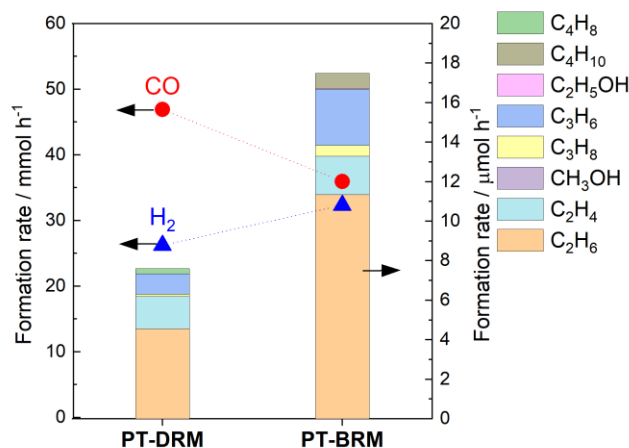


Figure 3.7 H₂ and CO formation rates (left-axis), and C₂₊ hydrocarbons (right-axis) of 7.5 wt% Co₅Ni₉₅@SiO₂(500) catalyst in PT-DRM and PT-BRM ($P = 25.0 \text{ W}$, $\Phi = 7 \text{ mm}$, spot position: Top, $F = 100 \text{ mL min}^{-1}$).

To obtain insight on the steam role, we investigated increasing steam flowrate from 7.4 to 14.6 mL min⁻¹ by raising the temperature of the H₂O trap (Figure 3.8). The H₂/CO ratio increased, and CO₂ conversion decreased with increasing the H₂O amount while the $\dot{r}_{syn}$ did not change significantly in 61–69 mmol h⁻¹ in these experiments. The increased H₂/CO ratio and decreased CO₂ conversion could be attributed to the promotion of the WGS reaction (eq. 3.8) by the increased water amount because the formed CO can convert to CO₂ based on eq. 6. C₂₊ formation rate of 20.1 μmol h⁻¹ was higher with small amount of H₂O (7.4 mL min⁻¹ at room temperature). The further increase in H₂O feed caused slight decrease in the C₂₊ formation rate to produce 15.1 μmol h⁻¹. The decrease in C₂₊ hydrocarbons with increasing H₂O amount could be

due to either the consumption of the formed CO by the WGS reaction to produce H₂ and CO₂, excessive coverage of the active sites by adsorbed H₂O [55, 56]. Other possibilities could be the oxidation of hydrocarbons or even the catalyst nanoparticles, especially when the oxidant concentration increased at this high temperature.

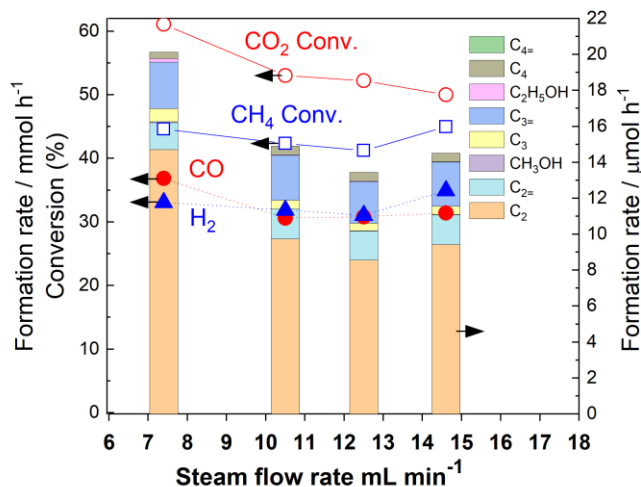


Figure 3.8 Results of activity tests of PT-BRM under different steam flowrate ($P = 25.0$ W, $\Phi = 7$ mm, spot position: Top, and $F = 100$ mL min⁻¹).

The 2D mapping of the surface temperature of the reactor during the PT-BRM reaction is shown in Figure 3.9, revealed that the large temperature gradient was formed from 178 to 1013 °C. The surface temperature progressively decreased when moving away from the center of the irradiated spot. This temperature distribution supports our assumption that CH₄ reforming and FTS reaction proceeds at the high- and low- temperature zones, respectively.



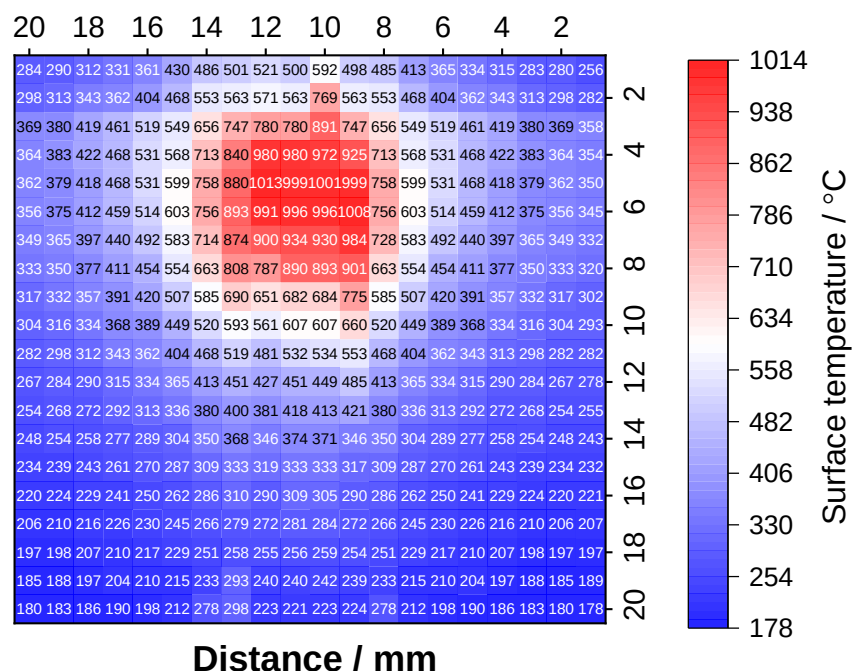


Figure 3.9 2D temperature map during PT-BRM in Figure 3.7.

To modulate the surface temperature, we varied the light power in the PT-BRM reaction. As shown in Figure 3.10, the C_{2+} formation rates were decreased with decreasing the light power while r_{syn} value was not changed significantly. In these experiments, we confirmed that maximum surface temperature of the reactor from 820 to 1013 °C. Unfortunately, we observed a damage occurred on the reactor surface during the activity tests at higher power values and smaller spot sizes (21.5 and 25 W, 7 mm) possibly due to the temperature around 1000°C (945 °C at 21.5 W, and 1013 °C at 25 W). To decrease the damage, the following activity tests were conducted at a light power of 18.2 W.

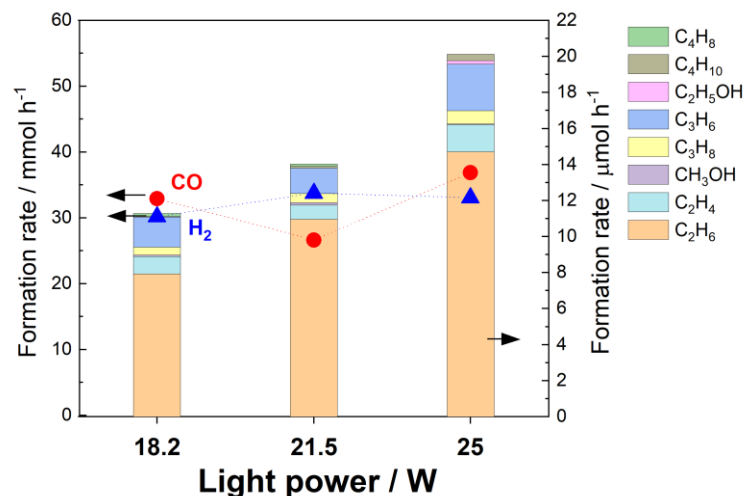


Figure 3.10 Results of activity tests of PT-BRM under different light power ($P = 18.2\text{--}25\text{ W}$, $F = 100$, Position: Top, $\Phi = 7\text{ mm}$).

To further explore the role of the partial pressures of CO_2 and CH_4 on the C_{2+} formation rates, we changed the flow rate of the Ar gas in PT-BRM. In the former activity tests, the gas ratio of $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}/\text{N}_2/\text{Ar}$ were 2/1/1/5 (Ar: 50 mL min^{-1}). In this experiment, we reduced the Ar flow rate from 50 mL min^{-1} to 0 mL min^{-1} (Figure 3.11). By reducing the Ar flow rate, C_{2+} formation rate increased remarkably. The results suggest that the partial pressure of the syngas is the reason for the profound formation of the C_{2+} hydrocarbons by removing the Ar dilution.

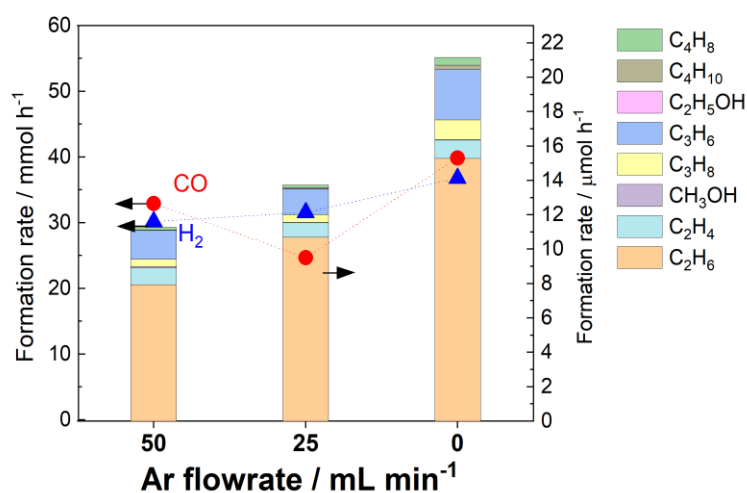


Figure 3.11 Effect of dilution with 50-, 25-, and 0- mL min^{-1} Ar ($P = 18.2\text{ W}$, $F = 100\text{-, }75\text{-, and }50\text{-mL min}^{-1}$).

To investigate the irradiance effect on the formation rates of C_{2+} hydrocarbons, we increased the diameter of the irradiated spot (Φ) from 7 to 11 mm (Figure 3.12). The $\dot{r}_{H_2}$ decreased from 42 to 22 mmol h^{-1} and the $\dot{r}_{CO}$ decreased from 38 to 8 mmol h^{-1} with increasing the spot diameter from 7 to 11 mm. The formation rates of C_{2+} hydrocarbons dropped to half using the larger spot of $\Phi = 11$ mm. The highest surface temperatures in $\Phi = 7$ mm and $\Phi = 11$ mm were 822 °C and 750 °C, respectively. The decrease in the syngas and C_{2+} hydrocarbons with $\Phi = 11$ mm could be ascribed to the lower surface temperature.

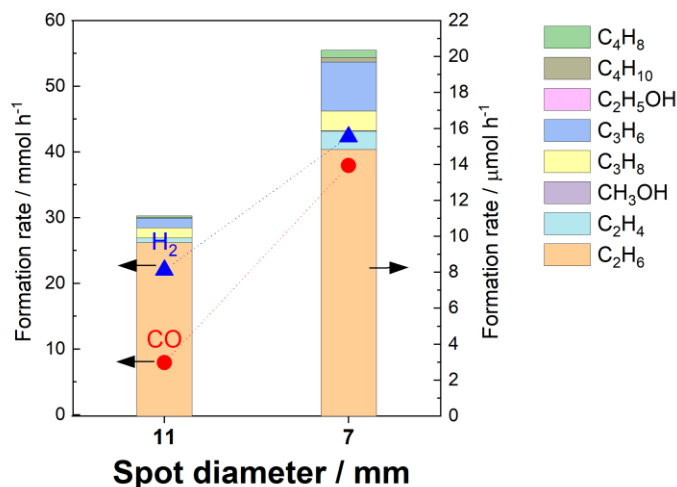


Figure 3.12 Effect of spot diameter at $P = 18.2$ W, $F = 50$ mL min^{-1} .

To investigate the effect of the high- and low-temperature zones downstream on the C_{2+} formation, the irradiation position was changed by irradiating the top, middle, and down positions of the flat reactor (Figure 3.13 shows the schematic representation). In these experiments, we used a spot size of 11 mm to avoid the reactor damage. The r_{syn} value was improved by irradiating the down position, which was consistent with our previous study.[22] At the lower temperature zone downstream from the light spot, the reverse reaction of DRM or BRM could happen, which reduces the r_{syn} value, as revealed in our previous work. The C_{2+} formation rates were drastically improved by irradiation the top position by 10 times compared to the down position, which support that the low-temperature zone catalyze FTS reaction (eq. 3.4–3.5).

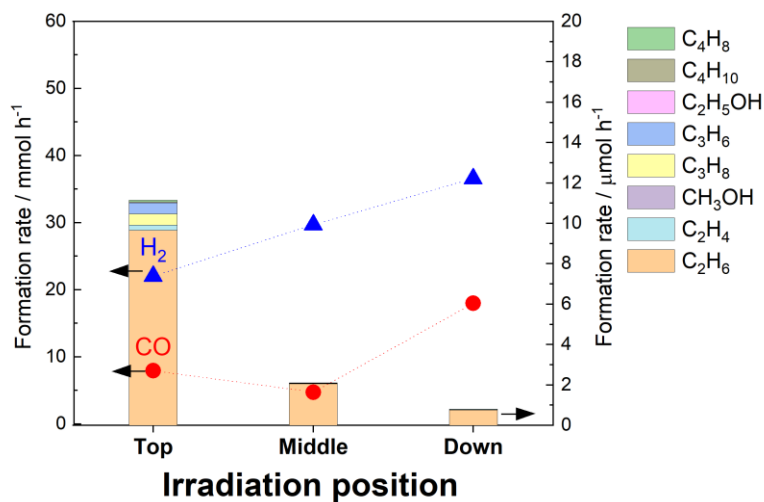


Figure 3.13 Effect of light irradiation position at $P = 18.2$ W, $\Phi = 7$, or 11 mm.

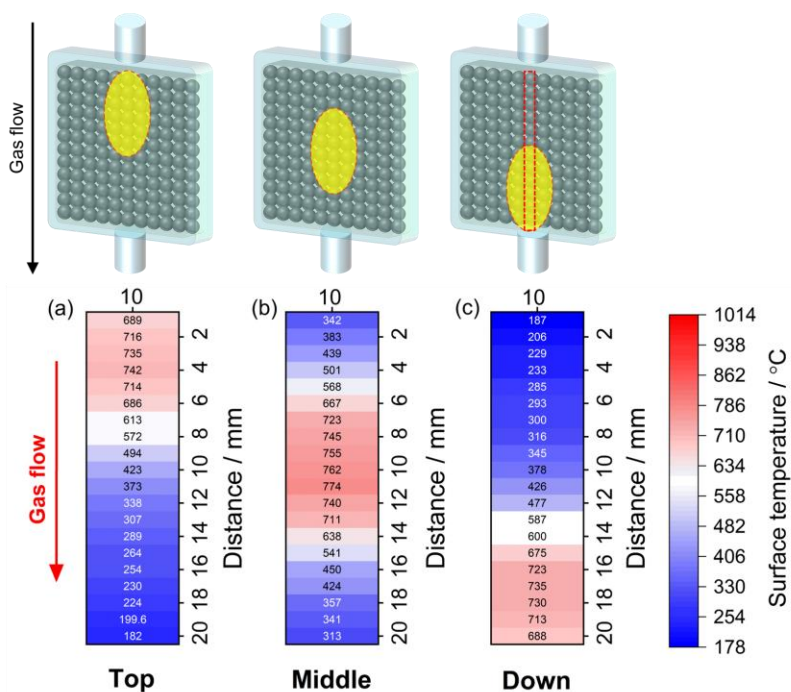


Figure 3.14 The schematic representation (above) and the surface temperature measurement region (represented by the dotted red rectangle). Surface temperature values (below) of the central axis of the reactor under $P = 18.2$ W, Position: Top (a), Middle (b), and Down (c).

The Effect of Crystallite Size and Pore Size Distribution

To investigate that role of the calcination treatment, at higher calcination temperature (550 °C) and longer time (6 h) was used to prepare the alloy catalyst, which was denoted 7.5 wt% $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2(550)$. The change of the calcination conditions increased the specific surface area from 157 (500 °C, 1 h) to 469 $\text{m}^2 \text{g}^{-1}$ (550 °C, 6 h) based on the N_2 adsorption-desorption isotherms (Figure 3.15a) while the crystallite size of alloy nanoparticles also increased from 3.7 to 9.3 nm. The 7.5 wt% $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2(550)$ had a higher uptake at around 2 nm in the pore size distribution plot (Figure 3.15b), which indicates meso- and micro-pores were formed with increasing the calcination temperature and time. In PT-BRM activity tests, the formation rates of syngas and C_2+ hydrocarbons increased substantially with increasing the calcination temperature and time (Figures 3.15c-d). The formation rates of C_2+ hydrocarbons in 7.5 wt% $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2(550)$ were 24.1 $\mu\text{mol h}^{-1}$, which were two times that in 7.5 wt% $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2(500)$ (i.e., 11.1 $\mu\text{mol h}^{-1}$), which suggests the pore-structure have a key role for the C_2+ formation.

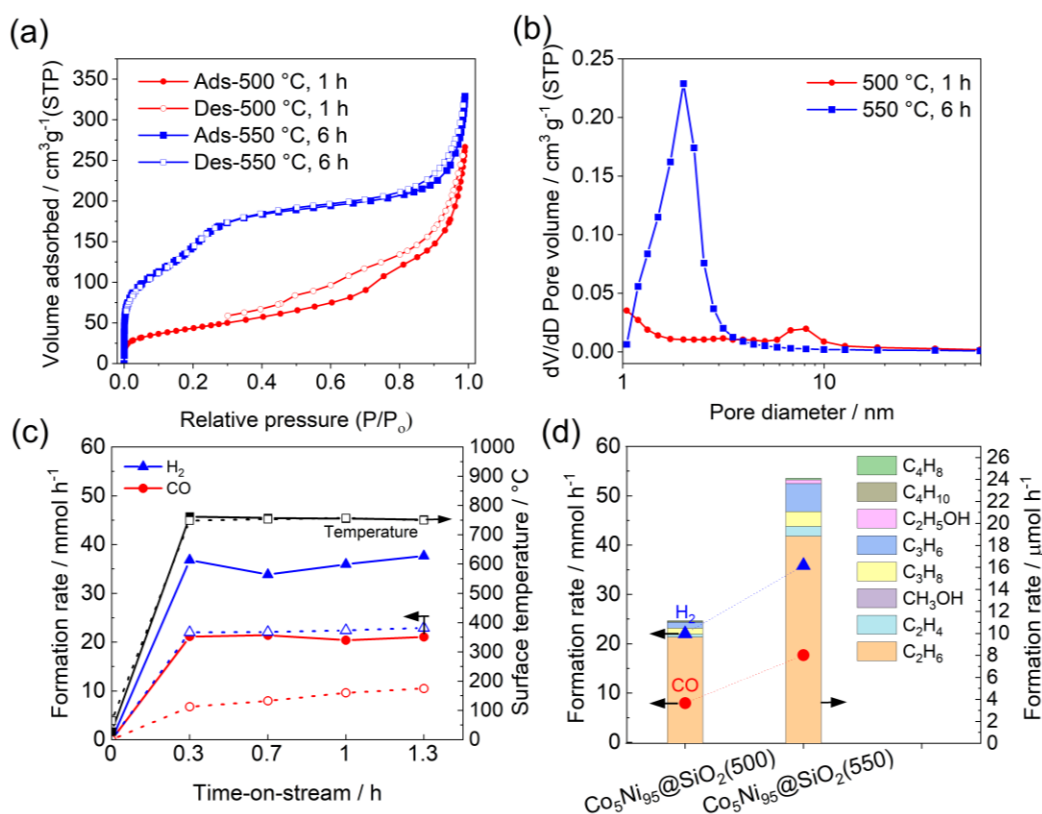


Figure 3.15 (a) Adsorption-desorption isotherms, (b) pore size distribution, (c) formation rates of H_2 , CO, and (right-axis) surface temperature of $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2(500)$ (dot line) and $\text{Co}_5\text{Ni}_{95}\text{@SiO}_2(550)$ (solid line) catalysts, and their C_2+ formation rates (d).

Synthesis of Metallic and Bimetallic Catalysts

To boost the C₂+ hydrocarbons production through the tandem catalysis process, we synthesized monometallic and bimetallic catalysts using Co, Ni, and Ru using the same procedure for the synthesis of the 7.5 wt% Co₅Ni₉₅@SiO₂(550) catalyst. The 7.5 wt% Co₅Ni₉₅, Co, or Ru/SiO₂ catalyst are excepted which were synthesized by impregnating 7.5 wt% metal on commercial silica for the FTS activity test. The XRD patterns of the calcined catalysts (Figure 3.16a) indicates the formation of NiO in Ni₁₀₀@SiO₂(550) catalyst, and Co–Ni oxide Co₅Ni₉₅@SiO₂(550) and Co₅₀Ni₅₀@SiO₂(550) catalysts. In Co₁₀₀@SiO₂(550) and Ru₁₀₀@SiO₂(550), the observed peaks were assignable to Co₃O₄ and RuO₂ respectively. These catalysts after calcination had similar N₂ adsorption-desorption isotherms (Figure 3.16b) and pore size distribution centered at 2 nm regardless of the metals (Figure 3.16c), which supports that porous structure of the SiO₂ shell is independent of the metal species.

Table 3.2 summarized the particle sizes, specific surface areas, total pore volumes, and metal contents of these catalysts. The pore size distribution of these catalysts showed similar microporous distribution each other around 2 nm regardless of the metal used, which is consistent to our assumption that SiO₂ shell has porous structure. The XRD patterns of the reduced catalysts matched the metallic phases (Figure 3.16d). Crystallite sizes in Table 1 indicated that the Co₅Ni₉₅@SiO₂(550) catalyst had the smallest of 13.4 nm among Co–Ni alloy samples compared to the monometallic Ni and Co samples, which agrees with our previous work.[22] In addition, the molar ratio of Co/(Co+Ni) were very close to the addressed values in the bimetallic Co₅Ni₉₅@SiO₂(550), and Co₅₀Ni₅₀@SiO₂(550) around 6.2 % and 51.0%, respectively. The H₂ pretreatment at 600 °C was sufficient to reduce the metal oxides based on the H₂-TPR profiles in Figure 3.14e. Based on the UV-Vis-NIR spectra (Figure 3.16f), all samples showed a strong light absorption in visible and near-IR range.

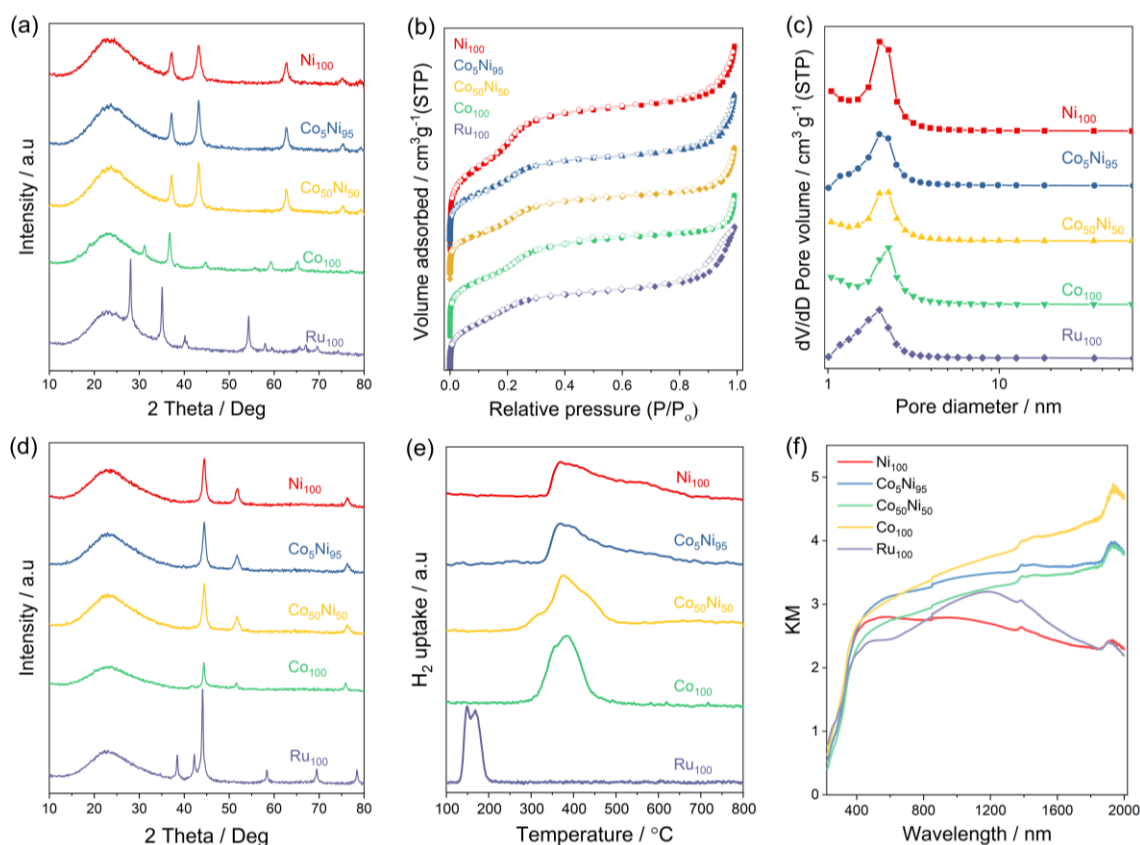


Figure 3.16 (a) XRD patterns, (b) adsorption-desorption isotherms, and (c) pore size distribution of the calcined catalysts at 550 °C for 6 h. (d) XRD patterns of the reduced catalysts at 600 °C. (e) H₂-TPR profiles of the calcined catalysts. (f) Diffuse reflectance UV-Vis-NIR spectra of the catalysts reduced at 600 °C.

Table 3.2. Physical properties of the prepared catalyst

Catalyst	$d_{\text{XRD}}^{[a]}$ / nm	$d_{\text{TEM}}^{[b]}$ / nm	$S_a^{[c]}$ / m ² g ⁻¹	$V_p^{[d]}$ / cm ³ g ⁻¹	Metal wt% ^[e]
Ni ₁₀₀ @SiO ₂ (550)	14.1	17.3	717	0.68	6.7
Co ₅ Ni ₉₅ @SiO ₂ (550)	13.4	9.3	469	0.51	5.3
Co ₅₀ Ni ₅₀ @SiO ₂ (550)	19.1	20.4	399	0.44	6.1
Co ₁₀₀ @SiO ₂ (550)	17.9	n.d. ^[f]	488	0.47	7.1
Ru ₁₀₀ @SiO ₂ (550)	17.9	3.9	503	0.51	6.9

[a] Crystallite size estimated from by XRD, [b] mean particle size estimated by TEM of reduced catalysts. [c] Specific surface area estimated by BET method from N₂ adsorption isotherm, [d] total pore volume obtained by the BJH method from N₂ adsorption isotherm of the calcined samples. [e] Metal wt% was quantified by ICP. [f] n.d.: Not determined.

Figure 3.17 shows TEM images and histograms of particle size distribution of the reduced catalysts. A broad particle size distribution was observed in the monometallic $\text{Ni}_{100}@\text{SiO}_2(550)$ catalyst. With the addition of small amount of cobalt (5 mol%) in $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(550)$, the particle size distribution slightly narrowed (Figures 3.17a and 3.17b) compared to $\text{Ni}_{100}@\text{SiO}_2(550)$ catalyst. The further increase in Co content result in the broad particle size in around 5–45 nm (Figure 3.17c). These trends are the same as our previous study [22], although the preparation method and metal content was slightly changed in the present study.

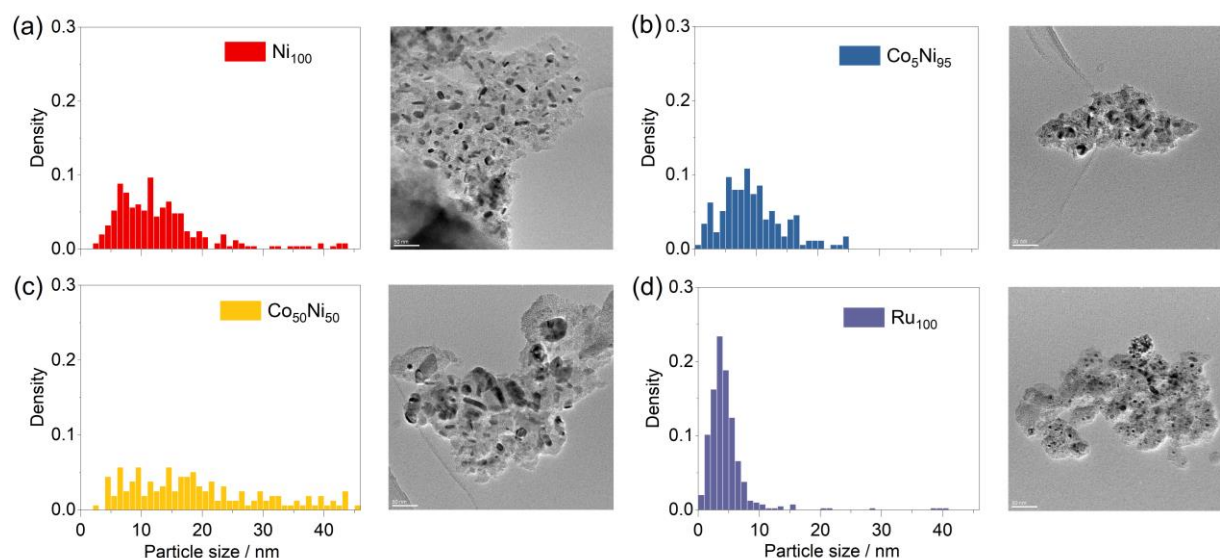


Figure 3.17 TEM images and histograms of the reduced catalysts (scale bar: 50 nm).

Activity Tests Using Single- and Dual-bed Layout

We investigated the formation rates of syngas and C_{2+} hydrocarbons in PT-BRM reactions using single- and dual-bed layouts using combinations of the prepared catalysts. In the single-bed experiments (Figure 3.18), $\text{Ni}_{100}@\text{SiO}_2(550)$ had syngas of $\dot{r}_{\text{CO}} = 19$, and $\dot{r}_{\text{H}_2} = 42 \text{ mmol h}^{-1}$ which was higher than the $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(550)$ catalyst that produced $\dot{r}_{\text{CO}} = 18$, and $\dot{r}_{\text{H}_2} = 36 \text{ mmol h}^{-1}$. On the other hand, the $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(550)$ catalyst showed higher C_{2+} formation rates around $24.1 \mu\text{mol h}^{-1}$ compared to the monometallic $\text{Ni}_{100}@\text{SiO}_2(550)$ catalyst (Figure 3.18a-b). The C_{2+} formation rates in $\text{Co}_{50}\text{Ni}_{50}@\text{SiO}_2(550)$ were much lower than that in $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2(550)$, which could be due to the rapid deactivation for the syngas formation (Figure 3.18c-d). In

Co₁₀₀@SiO₂(550), almost no activity was observed due to the oxidation of Co metal in the present reaction conditions (Figure 3.19).

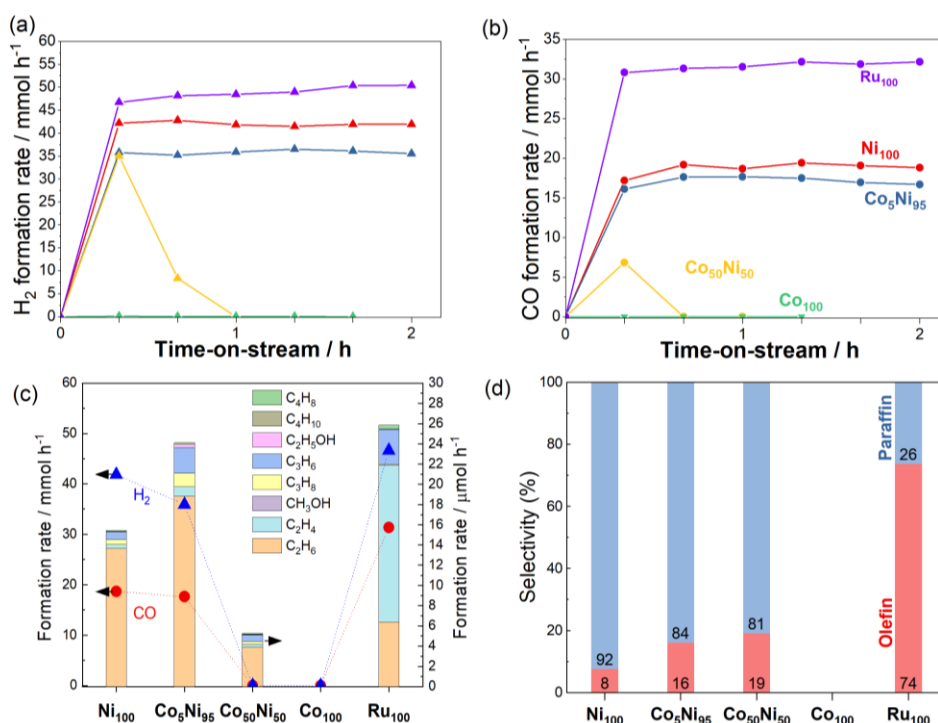


Figure 3.18 Activity test results of different catalysts in the single-bed arrangement. (a) Time-on-stream formation rates of H₂. (b) C₂⁺ formation rates at 1 h of activity test of M(I)_x M(II)_{100-x}@SiO₂(500). TOS C₂⁺ formation rates of (c) Co₅Ni₉₅@SiO₂(550) and (d) olefin and paraffin selectivity.

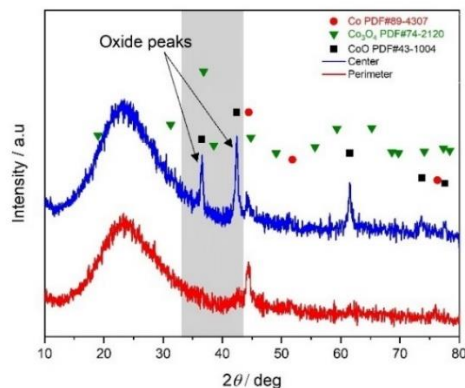


Figure 3.19 Photograph featuring the quartz reactor filled with Co₁₀₀@ SiO₂(500) after the PT-BRM activity test and XRD of the Co₁₀₀@SiO₂(500) after the PT-BRM activity test with the center of the irradiated spot (Blue) and the nonirradiated perimeter (Red).

Notably, the Ru₁₀₀@SiO₂ catalysts showed the higher formation rates for syngas and comparable initial activity in C₂⁺ formation rates (25.9 μmol h⁻¹) with the higher selectivity to ethylene (light blue one, 59.8%) and other olefins (Figure 3.18d). Co₅Ni₉₅@SiO₂(550) catalyst showed very stable syngas and C₂⁺ formation rates around up to 4 h of the activity test (Figure 3.20a) while maintaining high paraffin selectivity around 85%. The C₂⁺ formation rates on Ru₁₀₀@SiO₂(500) decreased to 9.4 μmol h⁻¹ after 3 h of reaction (Figure 3.20b).

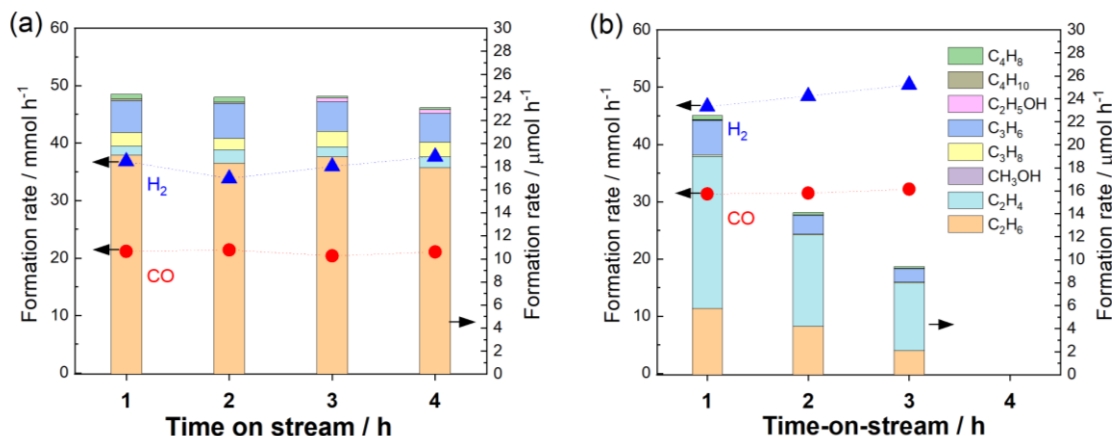


Figure 3.20 Time-on-stream activity test results of (a) Co₅Ni₉₅@SiO₂(550) and (b) Ru₁₀₀@SiO₂(500) catalysts in the single-bed arrangement.

Then, dual bed system was investigated, where the Co₅Ni₉₅@SiO₂(550) catalysts were placed on the upstream position due to the high formation rates for syngas and high stability and some catalysts were tested for the downstream positions (Figure 3.21a). The Co₅Ni₉₅@SiO₂(550) was chosen as a CH₄ reforming catalyst thanks to its stability and high formation rates. To remove the middle temperature zone (Figure 3.14a) that promotes the selectivity of methanation reaction rather than FTS, quartz sand (40 mg) was used as separator from the second bed. Any of combinations were ineffective for C₂⁺ formation compared to the single bed of Co₅Ni₉₅@SiO₂(550).-Nonetheless, using Co₅₀Ni₅₀@SiO₂(550) and Ru₁₀₀@SiO₂(550) in the dual-bed layout high olefin selectivity was produced around 47.4 and 55.8 % respectively (Figure 3.21b). These second bed catalysts showed similar selectivity to their single-bed experiments, which confirms the contribution of the second bed to the formation of C₂⁺. This is evident in their higher olefin selectivity compared to the relatively low olefin selectivity (16.2 %) of the Co₅Ni₉₅@SiO₂(550).

Based on the above results, we assumed that the BRM and FTS reactions promoted sequentially in single reactor and catalyst for the formation of C_{2+} as with tandem reaction system. To obtain insights for the assumption, several control experiments were performed. First, we connected the flat photo-reactor for PT-BRM to another tubular reactor externally heated at 300 °C, where the $Co_5Ni_{95}@SiO_2(550)$ catalyst (0.3 g) was used in the former photo-reactor and 10 wt% Co/SiO_2 (0.3 g) was adopted a typical FTS catalyst of (Figures 3.21c entries D and F). The FTS reaction proceeded at 300 °C and produced a 2-fold increase in the C_{2+} formation around $56.9 \mu\text{mol h}^{-1}$ even at ambient pressure compared to the $Co_5Ni_{95}@SiO_2(550)$ in entry A in Figure 3.21d. Separately, we confirmed thermal FTS reaction proceeded on the $Co_5Ni_{95}@SiO_2(550)$ and Co/SiO_2 catalysts for FTS was confirmed at 300 °C using syngas (H_2/CO : 1, total flow rate: 30 mL min^{-1}) as the reactant gas using the tubular reactor (Figure 3.21e(E-F)). The $Co_5Ni_{95}@SiO_2(550)$ catalyst showed higher catalytic activity than the Co/SiO_2 catalyst, which could be the reason behind the enhanced C_{2+} formation rate in the single-bed $Co_5Ni_{95}@SiO_2(550)$ catalyst compared to the dual bed system of the $Co_5Ni_{95}@SiO_2(550)$ and Co/SiO_2 catalysts (Figure 3.21a). Additionally, these results indicate that both the $Co_5Ni_{95}@SiO_2(550)$ and Co/SiO_2 catalysts promoted the FTS reaction even at ambient pressure.

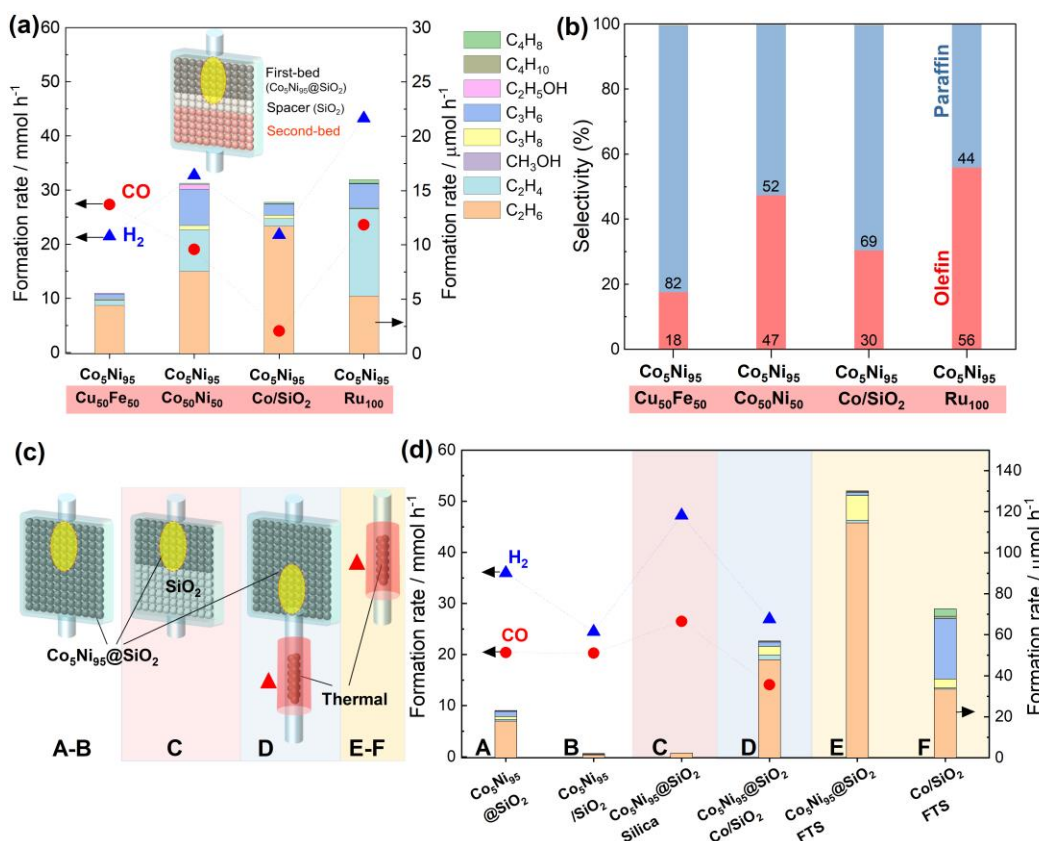


Figure 3.21 Activity test results of different catalysts in the dual-bed arrangement. (a) Formation rates of syngas (left-axis) and C₂₊ hydrocarbons (right-axis). (b) Olefin and paraffin selectivity at 1 h of activity test catalysts from figure 3.21a. (c) Schematic representation and (d) results of the control experiments in PT-BRM (entries A-D) and thermal FTS (entries E-F). (Conditions for A-D: $P = 18.2$ W, $\Phi = 11$ mm, spot position: Top, $F = 50$ mL min⁻¹). In entry D, a flat reactor irradiated at the down-position connected to a tubular reactor containing 10% Co/SiO₂ for thermal FTS. Entries E-F have Co₅Ni₉₅@SiO₂(550) and 10%Co/SiO₂ catalyst for thermal FTS heated by an external electric oven at 300 °C.

To further investigate the role of the temperature gradient on our tandem reaction system, we conducted activity tests of thermal BRM at 550, 650, and 750 °C using Co₅Ni₉₅@SiO₂(550) catalyst to minimize the temperature gradient. The syngas formation rates (Figure 3.22a) and the CO₂ and CH₄ conversions (Figure 3.22b) were drastically improved under the isothermal reaction conditions (with the external electric furnace). The formation rates of the C₂₊ hydrocarbons (Figure 3.22c) showed negligible values (0.2–0.4 μmol h⁻¹). The H₂/CO ratio decreased with increasing the temperature (Figure 3.22a) from 2.5 (550 °C) to 1.4 (750 °C), which followed the thermodynamic equilibrium [9]. Considering the above results and the fact that C₂₊ is more reactive than CH₄ in reforming conditions at high temperature [45], the C₂₊ formation in the current photothermal reaction system with a temperature gradient originated from tandem reaction

pathway composed of BRM at high temperature zone and FTS in low temperature zone (Figure 3.22d). We believe that the concept demonstrated here may open a new field in utilization of photo-formed temperature gradient for challenging catalytic reaction using single reactor system

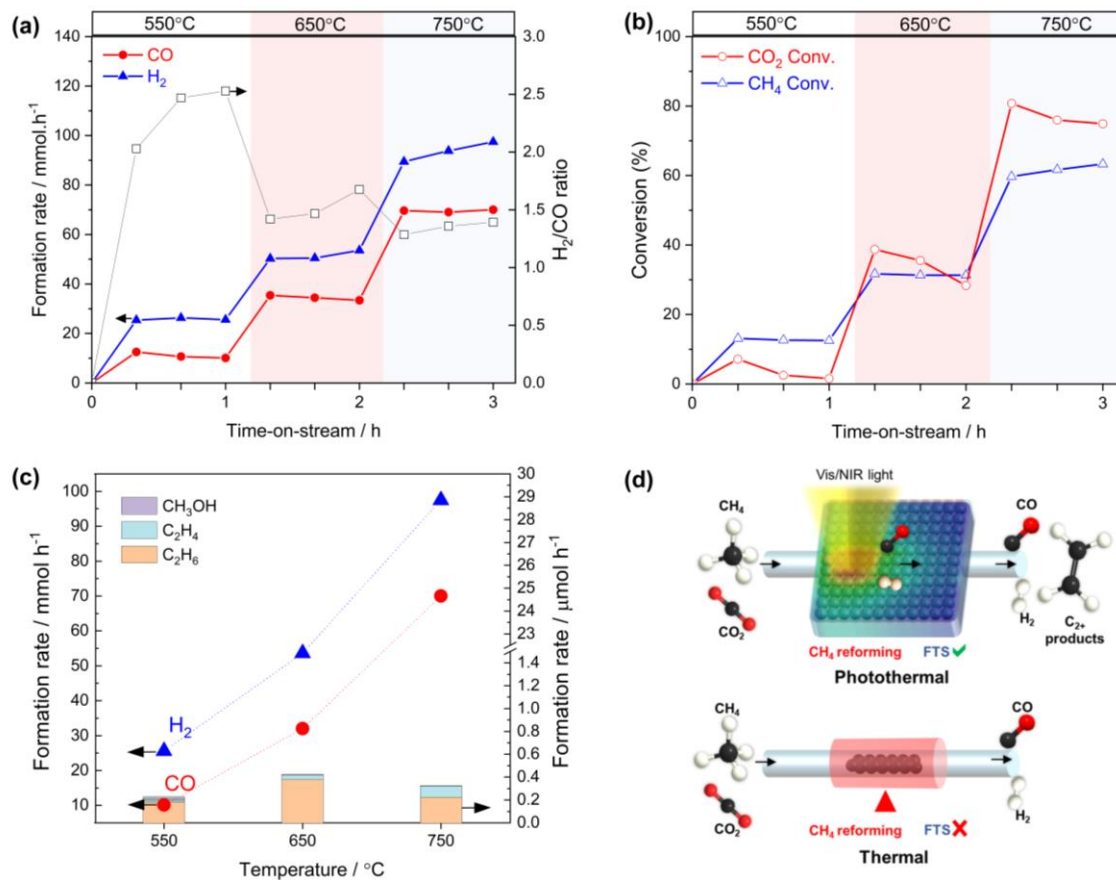


Figure 3.22 Thermal BRM activity test results (under dark) at 550-750 °C using 50 mg of Co₅Ni₉₅@SiO₂(550) in a tubular reactor with an inner diameter of 4 mm (a) H₂ and CO formation rates (left-axis), and H₂/CO (right-axis). (b). CH₄ and CO₂ conversions. (c) Syngas formation rates (left-axis), and C₂+ hydrocarbons (right-axis). (d) Schematic illustration of the photothermal tandem catalysis mechanism for CH₄ reforming and Fischer-Tropsch synthesis. Visible/NIR light is absorbed by the yolk-shell Co–Ni alloy@SiO₂ catalyst, generating localized heat that drives CH₄ and CO₂ conversion into syngas (H₂ + CO), followed by Fischer-Tropsch synthesis to produce C₂+ hydrocarbons. Arrows indicate the direction of flow of the reactant gas. The other reaction conditions were the same as Figures 3.7 of PT-BRM reaction.

Conclusion

The temperature gradient in the photothermal catalysis was frequently causes negative phenomenon as it promotes the backward and side reactions. Here, we successfully employed the temperature gradient to induce the tandem process of CH_4 reforming reaction and Fischer-Tropsch synthesis. The high-temperature zone directly irradiated promotes the highly endothermic CH_4 reforming, and down-stream low temperature zone catalyzes the successive Fischer-Tropsch synthesis reaction from syngas generated in the reforming process. The bi-reforming of methane was investigated to increase the H_2/CO ratio in the syngas products, and by changing the H_2O amount, the values was ranged in 0.90–2.2 in photothermal process. We revealed, using the suitable H_2/CO value for typical Fischer-Tropsch synthesis, the C_{2+} formation rate was enhanced. Strikingly, tunable selectivity of syngas and FTS products were achieved by controlling the reaction conditions and the catalyst species. To the best of our knowledge, this is the first report that demonstrates that tandem process of the CH_4 reforming and Fischer-Tropsch synthesis in single reactor with temperature gradient using photothermal catalysis. We believe this work paves the way for the further use of the photothermal catalysis in tandem reactions.

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Chapter 4

Novel Design of Gap Reactor for High-Performance Photothermal Methane Reforming

ABSTRACT

Photothermal catalysis has garnered significant attention as a potential solution to address energy scarcity. In photothermal catalysis, light irradiation directly heats the catalyst bed, inducing a localized temperature gradient. However, in methane reforming reactions such as dry reforming, the undesired reverse reaction typically proceeds in the lower temperature zone of the catalyst bed, which reduces the overall efficiency. To address this issue, we developed a novel flow-type photo-reactor composed of a quartz tube and a quartz filler welded within the tube. The narrow catalyst-filled gap was used for catalytic reaction that minimizes the temperature gradient under light irradiation. The developed reactor, termed gap reactor, demonstrated excellent catalytic performance in photothermal dry reforming of methane (PT-DRM), achieving ~70–80% conversion of CH_4 and CO_2 over 100 hours using a SiO_2 -encapsulated Co–Ni alloy catalyst previously developed by our group. Compared to the conventional quartz tube reactor with the same cross-sectional area for light absorption, the gap reactor significantly enhanced both conversion and stability. Furthermore, integrating the gap reactor with steam addition to the reaction feed successfully suppressed coke formation to only 0.6 wt% after approximately 50 hours of reaction. This study highlights the benefits of the gap reactor design in high-temperature catalytic applications up to 1000 °C.

Introduction

Greenhouse gases (GHGs), particularly methane (CH₄) and carbon dioxide (CO₂), are recognized as the major contributors to climate change, urging approaches to reduce their emissions. Dry reforming of methane (DRM, eq. 1) is proposed to reduce both CO₂ and CH₄ emissions in an energy-intensive reaction to produce syngas. However, the highly endothermic nature of DRM and low catalyst stability present challenges. Due to the thermodynamic limitation, high CH₄ conversion could be obtained at high temperatures over 800°C, where the temperature could be achieved by combustion of fossil fuel, similar to an industrial steam-reforming process, when constructing a large-scale process. [1, 2] This dependence on fossil fuels offsets the advantages of DRM by increasing the carbon footprint of this reaction.[3] Hence, solar-induced photothermal effect was proposed to drive this reaction without the combustion of fossil fuels. [4-8]



Photothermal catalysis has received significant attention due to global energy concerns. The photothermal effect can induce sufficiently high temperatures ranging from 800 to 1500 °C. [9-11] Therefore, photothermally-driven dry reforming of methane (PT-DRM) was proposed to achieve considerable CH₄ conversion.[4, 12-14] However, a temperature gradient, caused by non-uniform light distribution under focused light, poses key challenge in photothermal catalysis.[4, 11, 15, 16] This temperature gradient promotes the reverse reactions in the low-temperature zone of the catalyst bed.[15] Several recent studies investigated reaction systems that combine external heating with photothermal catalysis,[12, 17-19] these systems are likely to achieve more uniform temperature distributions. However, achieving stable and high CH₄ conversion in the PT-DRM reaction without external heating is still challenging. This raises the need for thorough studies to develop stable catalysts and optimum reactor design to maximize the CH₄ conversion under high irradiation fluxes. [4, 20, 21]

Temperature gradients not only decrease the conversion efficiency, but also severely compromise the catalyst stability. Although the high temperatures would benefit the reaction rate and conversion in PT-DRM, they can cause significant sintering of the catalytically active metal nanoparticles. [22-25] In addition, the catalysts in the low-temperature zone promotes coke

deposition due to the thermodynamic preference[15] via side reactions such as CH₄ decomposition (eq. 2), Boudouard reaction (eq. 3).



Therefore, it is crucial to develop stable catalysts with high resistances to sintering and coke deposition. We previously reported that Co–Ni alloy nanoparticles encapsulated in porous SiO₂ yolk shell (Co–Ni@SiO₂) exhibited improved activity and enhanced stability for the PT-DRM reaction, compared to the monometallic Ni@SiO₂ catalyst or impregnation catalyst without a SiO₂ shell.[15]

From the reactor design perspective, several studies have proposed new designs of photo-reactors.[5, 20, 21] For example, a double-tube type photo-reactor with vacuum thermal insulation and a selective solar absorbing coating was employed to achieve high temperature for CO₂ methanation under light irradiation.[26] Additionally, a reflective multi-pass photoreactor composed of a tube reactor and solar concentrator was also reported as a low-cost and highly effective photoreactor without the need for sun tracking for application under irradiation conditions.[20] These examples highlight the importance of reactor design from both fundamental and application-oriented perspectives. Inspired by these studies, we hypothesized that minimizing the temperature gradient has the potential to enhance the performance of the photothermal CH₄ reforming reaction in high-temperature conditions. Herein, we developed a novel flow-type photo-reactor consisting of a quartz tube and a quartz filler welded inside the tube, with the catalyst positioned in the gap between them (referred to hereafter as the "gap reactor", Figure 1a). The decrease in the thickness of the catalyst layer could contribute to a decrease in the temperature gradient. The developed gap-reactor provided superior performance in CH₄ conversion through dry- and bi-reforming reactions using the Co–Ni@SiO₂ catalyst.

Experimental

Catalyst Synthesis

The Co–Ni alloy nanoparticles encapsulated with porous SiO₂ yolk shell was prepared two step method according to the previous report [15] with slight modification. First, Co₅Ni₉₅ hydroxide nanoplatelets were prepared by hydrothermal treatment, and then encapsulated with a SiO₂ shell. Briefly, a solution of pre-dissolved polyvinylpyrrolidone (PVP, 3 g) solution in deionized water (DIW, 120 mL) was mixed with 0.3 mmol of Co(NO₃)₂·6H₂O and 5.7 mmol of Ni(NO₃)₂·6H₂O solutions under Ar flow. After stirring for half an hour, 30 mL of NaOH were added dropwise over 30 minutes. After that, the mixture solution was transferred to an autoclave lined with Teflon to be hydrothermally treated at 150 °C for six hours. The resulting slurry was decanted three times with DIW after it had cooled to room temperature.

After dispersing the Co₅Ni₉₅ nanoplatelets suspension in 150 mL of DIW, 300 mL of ethanol and 15 mL of NH₃ (aq) were added. Separately, cetyltrimethylammonium bromide (CTAB, 2.7 g) was dissolved in ethanol/DIW (40 mL, 1/1, vol%) Then, 15.5 mL of tetraethyl orthosilicate (TEOS) and the CTAB solution were simultaneously added dropwise to the nanoplatelets suspension. After vigorously stirring the mixture for one hour, it settled down. After the 250 mL supernatant was decanted, the 200 mL suspension was dried at 80 °C using water bath and then kept in oven overnight at 80 °C to remove any remaining solvents. The catalyst was calcined at 500 °C at the heating rate of 10 °C min⁻¹.

New Reactor Design

A flow-type photo-reactor was designed to increase the catalyst temperature for PT-DRM effectively and minimize the temperature gradient. In this reactor, quartz fillers were welded inside quartz tube reactors with an inner diameter of 10 mm, respectively (Figure 4.1). In the flat-type quartz reactors used in our previous study [15], controlling the thickness of the catalyst bed and light irradiation area was limited by its manufacturing process. The advantage of this gap reactor lies in its ability to regulate the catalyst space through the shape of the internal filler. In this study, three reactors with gap thicknesses of 1, 2, and 3 mm were used for catalyst filling and are referred to as *x*-mm-gap reactors, where *x* is the gap thickness. Note that, in these reactors, the cross-sectional area of the catalyst exposed to light (Figure 4.2). changes with variations in the gap

thickness (Figure 4.1). Moreover, the light penetration depth of the thin pellet of the reduced catalyst was $< 200\ \mu\text{m}$, indicating that only a limited zone at the top of the catalyst granules is directly heated by light irradiation. For the control experiments, quartz tube reactors with inner diameters of 4 and 8 mm (Figure 4.1) were used, where the cross-sectional area in the 2-mm-gap reactor matched that of the 8-mm-tube reactor. The structural information for the reactors used in this study is summarized in Table 4.1.

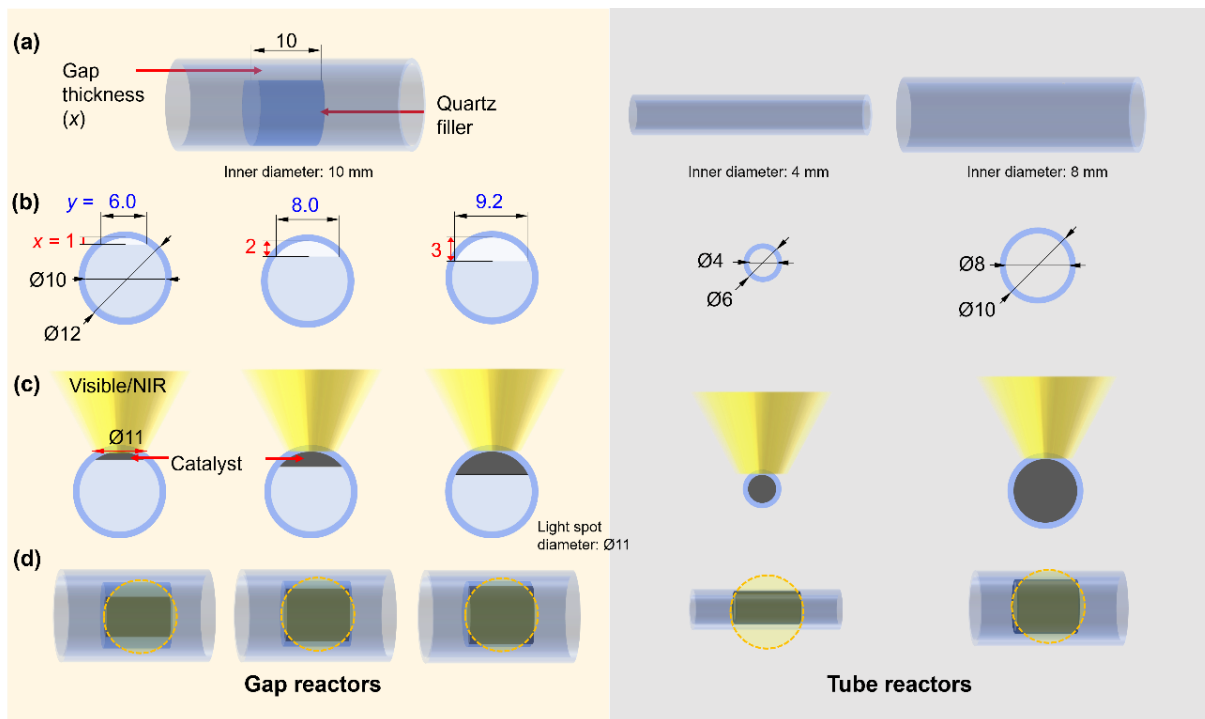


Figure 4.1 Schematic representation of the photo-reactors used in this study. (a): Overview. (b): Side view. (c): Side view with catalyst. (d): Top view with catalyst. The light spot diameter of 11 mm Φ is used for the representation. Dimensions are in mm.

Table 4.1 Information of the reactor used in this study.

Reactor	Catalyst bed volume / mL	Catalyst bed length / mm	Catalyst weight / mg	GHWV ^[1] / L g ⁻¹ h ⁻¹
1-mm-gap	0.04	10	35	3.4×10^2
2-mm-gap	0.11	10	60	2.0×10^2
3-mm-gap	0.20	10	110	1.1×10^2
4-mm tube	0.13	10	60	2.0×10^2
8-mm tube	0.50	10	340	3.5×10^1

^[1] Gas hourly weight velocity. The total flow rate was 200 ml min⁻¹.

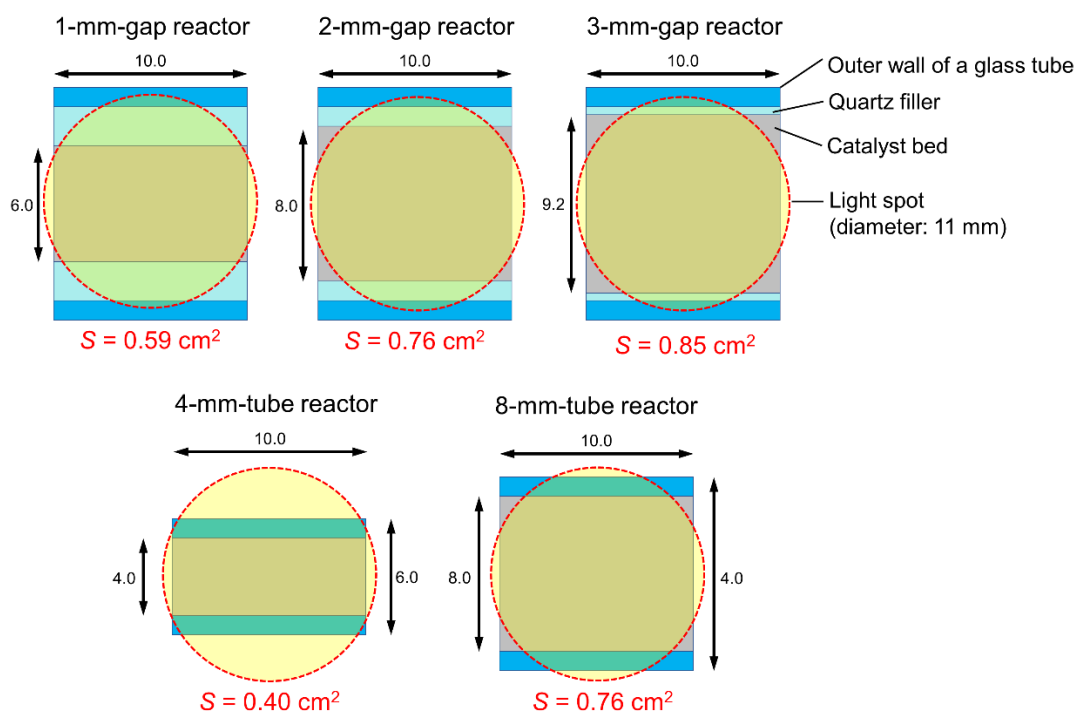


Figure 4.2 Top view of the reactors under light irradiation with a spot diameter of 11 mm. The cross-sectional area for light absorption (S) was calculated from the overlap between the catalyst zone and the light spot.

Characterization

The specific surface area was estimated from the amount of N₂ adsorption at 77 K using BEL-MAX-G instrument (MicrotracBEL, Japan), and the porosity of the catalysts was assessed via the Barrett–Joyner–Halenda (BJH) method. X-ray diffraction (XRD) measurement was carried out at room temperature using a Shimadzu LabX XRD-6000 with Cu K α radiation (40 kV, 30 mA). The crystallite size was determined by the Scherrer equation using the full width at half maxima (FWHM) of the diffraction line at $2\theta = 44.8^\circ$. Transmission electron microscopy (TEM) was conducted using a JEM-2200SF and JEM-ARM200F equipped devices (JEOL, Japan). UV-Visible Diffuse reflectance spectra (DRS) was recorded on a JASCO V-570 spectrophotometer with a BaSO₄ reference. The amount of deposited coke after PT-DRM reaction test was determined using the elemental analysis with CNH analyzer (MT-5 and MT-6, Yanaco Analytical Systems, Japan) and Micro analyzer (JM-10 and JM-11, J Science Lab, Japan).

Catalytic Activity Tests

Photothermal and thermal activity tests were carried out under ambient pressure using a fixed-bed continuous-flow system. The powder of the Co₅Ni₉₅@SiO₂ catalyst was ground into 150–300 μm granules after pelletization at 40 MPa. The reactors with 1, 2, and 3-mm gap thicknesses were filled with 35, 60, and 110 mg of the granules, respectively (Table 4.1). The tubular reactors with inner diameters of 4 and 8 mm filled with 60 mg and 340 mg of the catalyst granules, respectively.

Before the activity test, the catalyst was pre-treated in an 100% O₂ gas flow (5 mL min⁻¹) at 450 °C for 30 minutes to remove organics, and then reduced for 30 minutes at 600 °C using an 10% H₂/Ar gas (100 mL min⁻¹), followed by cooling to room temperature under an Ar flow. In the PT-DRM and PT-BRM reactions, gas compositions were CH₄(22.5 mL min⁻¹)/CO₂(22.5 mL min⁻¹)/N₂(10 mL min⁻¹)/Ar(145 mL min⁻¹) and CH₄(22.5 mL min⁻¹)/CO₂(12.0 mL min⁻¹)/H₂O(11.0 mL min⁻¹)/N₂(10 mL min⁻¹)/Ar(145 mL min⁻¹), respectively, unless otherwise stated. A 300 W Xe lamp with a 435 nm cut-off filter and a focusing lens were used for the light irradiation. A thermal power sensor (S425C-L, Thorlabs Inc., USA) to measure the light power. The power (P) and diameter of the irradiated spot (Φ) were changed by altering the current of the power supply and the distance between the light source and reactor, respectively. In thermocatalytic activity tests, the catalyst was heated in a tubular electric furnace without light irradiation.

The gas products were quantified by a gas chromatograph (GC) with thermal conductivity detectors. The conversion rates of the reactants (r_x : $x = \text{CH}_4$ or CO_2) and formation rates of the products (r_y : $y = \text{CO}$ or H_2) were calculated using relative calibration factors of each gas to an internal standard of N_2 . Conversion of x was obtained according to equations 4.4-4.5.

$$\text{Conversion of } x (\%) = (F_{x,\text{in}} - F_{x,\text{out}}) / F_{x,\text{in}} \times 100, \quad (4.4)$$

where $F_{x,\text{in}}$ and $F_{x,\text{out}}$ are the flow rate of x in the inlet and outlet gases, respectively. The following equation was used to calculate the light to chemical conversion efficiency (η):

$$\eta (\%) = [r_{\text{H}_2} \Delta_c H^\circ_{\text{H}_2} + r_{\text{CO}} \Delta_c H^\circ_{\text{CO}} - r_{\text{CH}_4} \Delta_c H^\circ_{\text{CH}_4}] / P \times 100, \quad (4.5)$$

where $\Delta_c H^\circ_x$ and $\Delta_c H^\circ_y$ are combustion enthalpies of x or y , respectively.

The conversion and H_2/CO ratio in chemical equilibrium in the present gas compositions were calculated by the NASA CEA program.[27]

4.3 Results and Discussion

4.3.1 Characterization

Figure 4.3 shows the characterization results of the prepared Co–Ni@SiO₂ catalyst. We checked the catalyst porosity by N₂ adsorption-desorption measurements as it was a crucial factor for the catalyst activity and stability in our previous study on PT-DRM [15]. The catalyst had type IV isotherm as shown in Figure 4.3a, and the specific surface area calculated by the BET method was 93 m² g⁻¹. The pore size distribution showed bimodal pore distribution around < 2 nm and 10 nm (Figure 4.3b). The XRD patterns of the samples after calcination and reduction pretreatments indicated the Ni(Co)O phase with rock-salt structure was transformed to the metallic phase upon reduction at 600 °C (Figure 4.3c). The crystallite size of the metallic phase was estimated to be 11.0 nm using the Scherrer equation. The spent catalyst maintained the metallic phase after the 2 h PT-DRM activity test using the 3-mm gap reactor with a slight increase of the crystallite size to around 16.1 nm. Based on TEM images in Figure 4.3d, the metal nanoparticles were encapsulated with the SiO₂ shell. The mean particle size of 13.5 nm (Figure 4.3e) was consistent with the crystallite size by XRD. The diffuse reflectance spectra (Figure 4.3f) showed enhanced light absorption property upon reduction treatment.

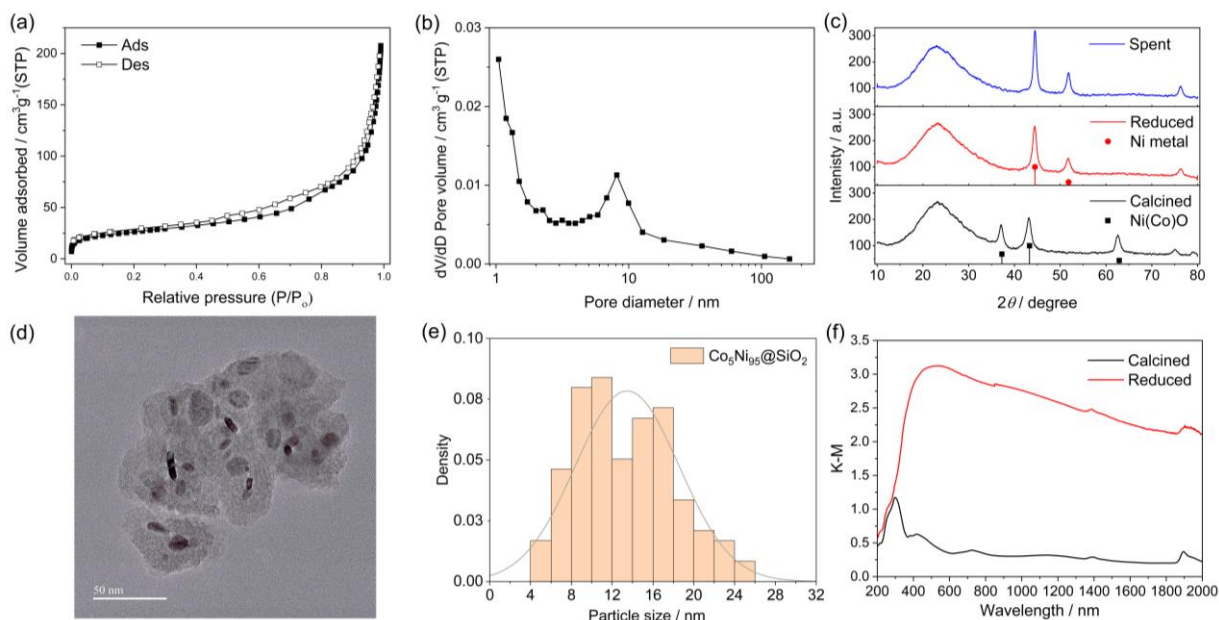


Figure 4.3 Characterization results of the Co₅Ni₉₅@SiO₂ catalyst: (a) adsorption-desorption isotherm, (b) pore size distribution of the calcined sample. (c) XRD patterns of the calcined,

reduced and spent catalyst. (d-e) TEM image and particle size distribution of the reduced catalyst. (f) The diffuse-reflectance spectra of the calcined and reduced samples.

4.3.2 Activity test results

Effect of Light Power

First, we investigated the effect of the gap thickness (1, 2, and 3 mm) on the catalytic performance at the light spot diameter of 11 mm under various light power conditions. For all gap thicknesses, the surface temperature of the reactor and formation rates of H₂ and CO (r_{H_2} and r_{CO}) increased with the increase in light power (Figures 4.4a- b). A similar trend was observed in our previous study on thermal and photothermal DRM reactions [15], where increased reaction temperature typically enhances the catalytic performance. The 2-mm-gap reactor showed higher r_{CO} and r_{H_2} values at all light power values (18–25 W) compared to the 1-mm-gap and 3-mm-gap reactors. The surface temperature of the reactor increased with the gap thickness from 1 to 2 mm, likely due to the larger cross-sectional area of the catalyst zone available for light absorption (Figures 4.1 and 4.2). Notably, the 1-mm-gap reactor achieved significantly higher formation rates of H₂ and CO at a light power of 25 W even at a low surface temperature of 686 °C, compared to the 3-mm-gap reactor (surface temperature: 811 °C), as shown in Figure 3a. These results highlight that the positive effect of reducing the gap thickness. On the other hand, at the gap-thickness of 3 mm, the formation rates of H₂ and CO decreased compared to that of 2 mm despite the similar surface temperatures across all light power levels. Based on these results, we concluded that 2-mm-gap is optimum for PT-DRM at the present reaction conditions.

Additionally, the H₂/CO ratio was lower than the stoichiometric value in DRM (*i.e.*, 1, eq. 1, Figure 4.4b, right axis). This could be interpreted by the simultaneous occurrence of side reactions such as reverse water gas shift reaction (eq. 6).



Furthermore, the H₂/CO ratio increased with the increasing light power in all gap reactors, although the difference was slight in the 2-mm-gap and 3-mm-gap reactors. The trend is likely attributed to the thermodynamic equilibrium because H₂/CO ratio increases at higher temperatures

(Figure 4.4d). The light-to-fuel conversion efficiency (η) in the 2-mm-gap reactor was 6.0 % at 25 W at the conversion range of approximately 60%.

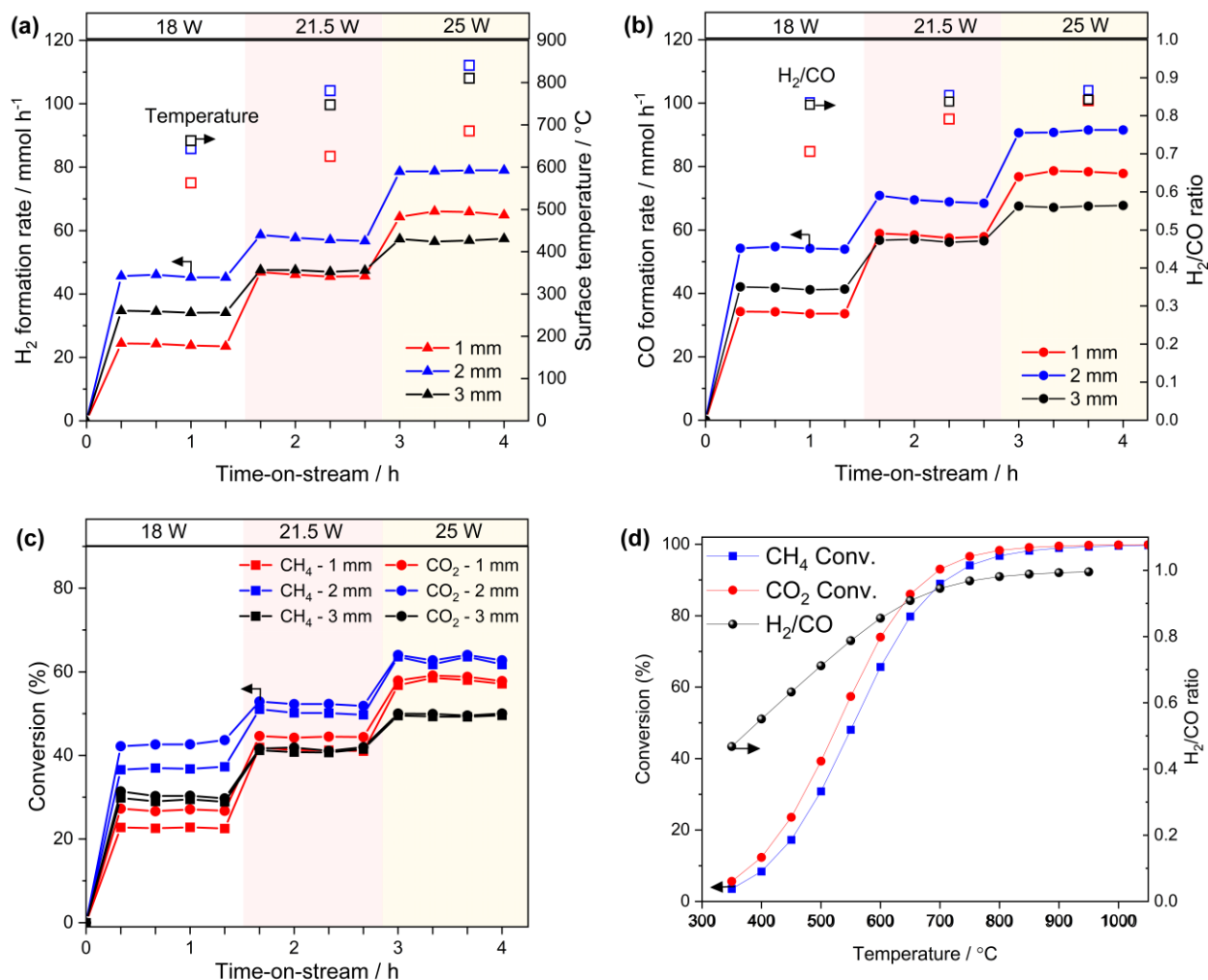


Figure 4.4 Results of photothermal catalytic activity tests using 1-, 2-, and 3-mm-gap reactors ($P = 18, 21.5$, or 25 W, and $\Phi = 11$ mm). (a): H₂ formation rate, (b): CO formation rate, and (c): conversion of CH₄ and CO₂. (d) Chemical equilibrium conversion and H₂/CO ratio of DRM reaction calculated by the NASA CEA program.

To investigate the performance of this reactor system in the absence of light irradiation, we conducted thermal DRM activity tests using electric furnace from 500 to 700 °C. In these tests, we used the 2-mm-gap reactor and tube reactor (inner diameter: 4 mm) without altering the catalyst amount (60 mg) and the reaction gas feed. The formation rates of H₂ and CO (Figure 4.5) and conversions of CH₄ and CO₂ increased with rising the reaction temperature. Moreover, as the reaction temperature increased, the H₂/CO ratio increased, which was consistent with the

photothermal activity test using in 1-mm-reactor (Figure 4.4b, c, right axis) and was not observed in 3-mm-gap reactor. This comparison suggests that, at the increased gap thickness of 3 mm, reverse or side reactions proceeded at the lower temperature zone of the back side of the reactor.

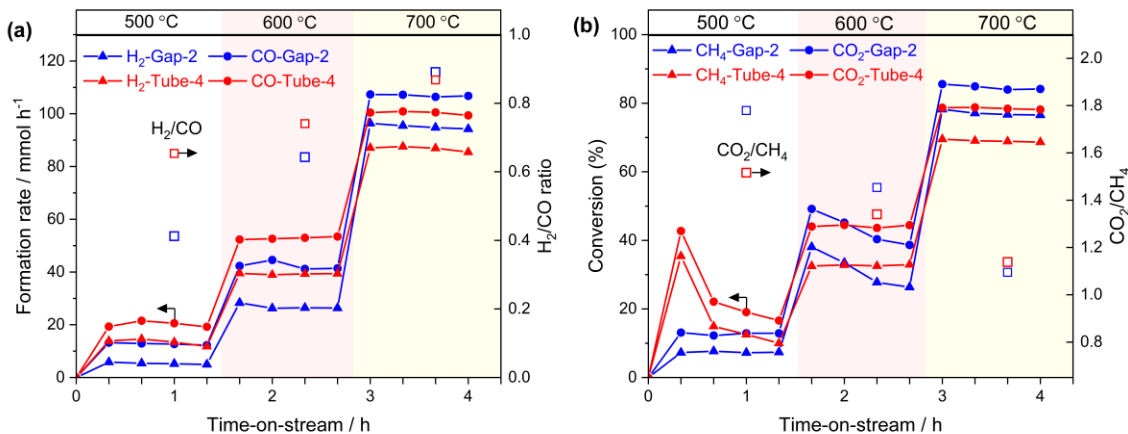


Figure 4.5 Results of thermal DRM activity tests using 2-mm-gap reactor, and 4-mm tube reactors under 500, 600, and 700 °C. (a): Formation rates of H₂ and CO, and H₂/CO (right-axis). (b): Conversion of CH₄ and CO₂, and converted ratio of CO₂ to CH₄ (*i.e.*, CO₂/CH₄).

Spot Diameter and Position

The irradiated spot diameter and position significantly affects the temperature distribution and reaction efficiency. [15, 28] We investigated the effect of spot diameter at a light power of 25 W. The formation rates of H₂ and CO increased with decreasing the spot diameter across all gap thicknesses (Figure 4.6a), accompanied by an increase in surface temperature (Figure 4.6b, right axis). The results indicate that the decreased spot diameter from 11 to 7 mm (*i.e.*, increased light flux) positively influenced the performance. The cross-sectional area for the light absorption decreased from 0.76 to 0.38 cm² with a decrease in the spot diameter from 11 to 7 mm in the case of the 2-mm-gap reactor. Considering that the increased cross-sectional area can positively contribute to the rise in temperature, the increased temperature and performance originate from the increased light flux in the present conditions.

The impact of the temperature gradient perpendicular to light irradiation direction on the catalytic activity was evaluated using the 2-mm gap reactor by irradiating different positions of the catalyst bed with a 7-mm-spot (Figure 4.7a). Light irradiation to the middle and downstream positions resulted in slightly higher formation rates of CO and H₂ compared to the upstream

irradiation (Figure 4.7b). We previously reported irradiation to downstream position produced twice the conversions and formation rates compared with irradiating the upstream position using flat type reactor (irradiation area: 20 mm $\times$ 20 mm, thickness: 1 mm, light spot diameter: 7 mm Φ).[15] The difference in the performance was attributed to the reverse reaction being promoted at a low-temperature downstream zone when the upstream zone was irradiated. [15] In the present experiment, the size of the irradiation area (8 mm $\times$ 10 mm, Figure 4.1) was nearly consistent with the light spot diameter (7 mm Φ), which is likely to reduce the positional effect of the light spot on the catalytic activity. It is worth mentioning that the cross-sectional area of the catalyst zone in the gap reactor is easily adjusted by modifying the inner diameter of quartz tube and the size of the inner filler. This flexibility provides a significant advantage in avoiding the mismatches of the light absorbing area and the light spot.

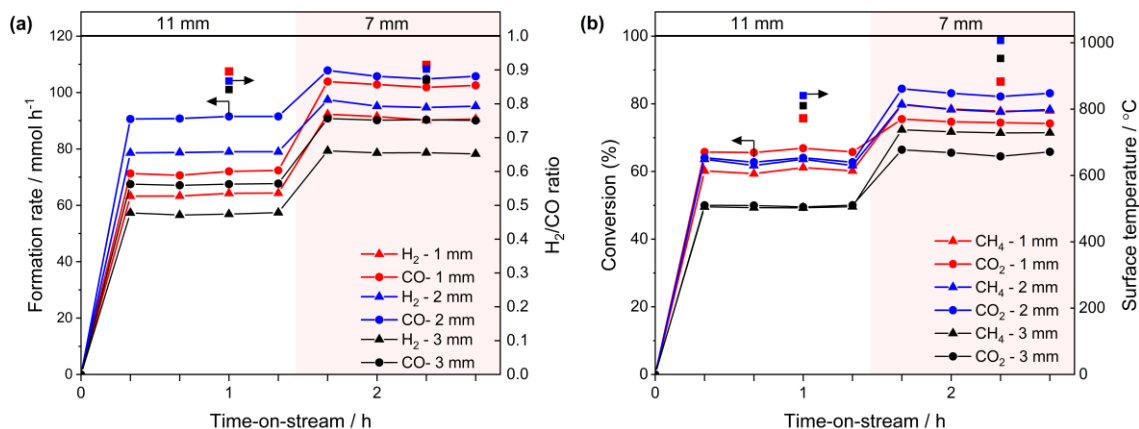


Figure 4.6 Results of activity tests using 1-, 2-, and 3-mm-gap reactors ($P = 25$ W, and $\Phi = 11$ or 7 mm). (a): formation rates of H_2 and CO , and H_2/CO (right-axis). (b): Conversion of CH_4 and CO_2 , and surface temperature (right-axis).

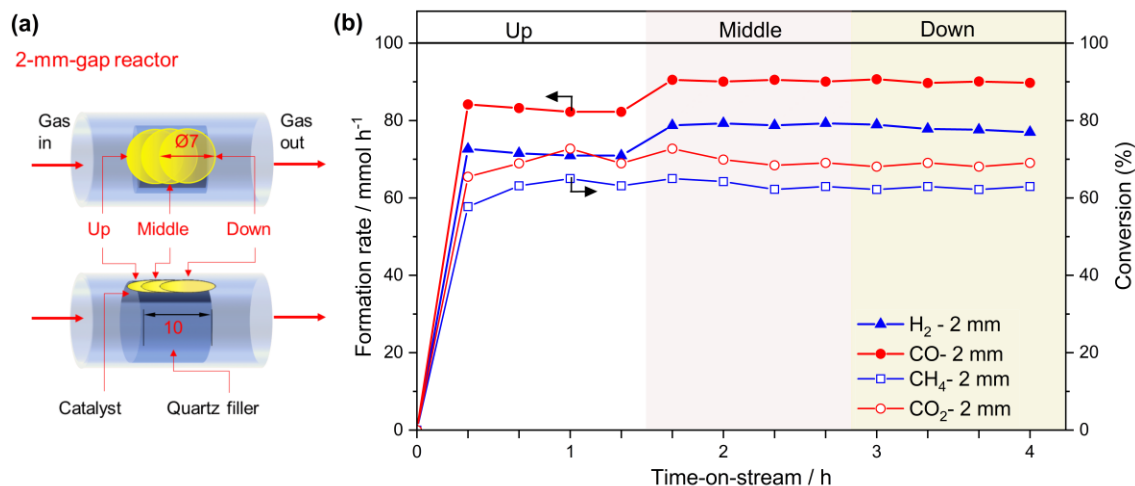


Figure 4.7 Effect of position of light spot on the photothermal catalytic activity. (a): schematic representation. (b): Formation rates of H₂ and CO (left-axis) and conversion (right-axis) of CH₄ and CO₂ using the 2-mm-gap reactor. ($P = 25$ W, $\Phi = 7$ mm.)

Comparison with tubular reactors in long-time reaction

The long-time stability of the catalytic systems was examined using the 2-mm-gap reactor and tubular reactor (inner diameter: 8 mm), with catalyst amounts of 60 and 340 mg, respectively (catalyst length: 10 mm). The 2-mm-gap reactor demonstrated excellent catalytic performance of ~78% CO₂ conversion and ~72% CH₄ conversion over 100 hours during PT-DRM (Figure 4.8a). The temporal decrease of the performance was observed in 10–20 hours of PT-DRM, which aligns with previously reported phenomena in thermal DRM reactions, and it is likely attributed to coke deposition [29–31]. In contrast, the 8-mm-tube reactor, with the same cross-sectional area for light absorption as the 2-mm-gap reactor, exhibited significantly lower conversion levels, with ~60% for CO₂ and ~50% for CH₄ (Figure 4.8b). The GHWV value in the 8-mm-tube reactor is 5.7 times lower than that in the 2-mm-gap reactor. These results emphasized the effectiveness of reducing the catalyst bed thickness to enhance performance in PT-DRM. To the best of our knowledge, the conversion level achieved in this study is the highest reported for systems utilizing a low-power light source, such as 300–500 W Xe lamps, without external heating, summarized in Table 4.2.[15–17, 32–37] Note that higher CH₄ conversion levels have been reported in PT-DRM when using high-power Xe lamps (e.g., 3 kW [38] or 6 kW [39]). Separately, the existence of a temperature gradient ($> \text{approximately } 200$ °C) was confirmed using thermocouples under a flow of inert gas, even in the case of the 2-mm-gap reactor. These results indicate that the gap reactor mitigated the

temperature gradient, resulting in high conversion even under relatively low light irradiation conditions by suppressing the reverse reaction at the low-temperature zone. Additionally, we confirmed that the conversion of CO₂ and CH₄ was approximately 60 % when using the 4-mm-tube reactor, where the same catalyst amount and bed length were employed as used in the 2-mm-gap reactor.

Coke formation is one of the crucial challenges in PT-DRM. Based on elemental analysis, the amount of deposited coke after 100-hour-reaction was 17 mg (28.3 wt%) in the 2-mm-gap reactor and 115 mg (33.8 wt%) in 8-mm tube reactor. The reduced coke formation can be attributed to the decreased temperature gradient because the coke formation is thermodynamically favorable at lower temperatures.

The addition of steam into the reaction feed in DRM (*i.e.*, bi-reforming) is effective strategy for reducing the coke formation and controlling the H₂/CO ratio in the produced syngas.[40, 41] To check the applicability of this gap reactor, we conducted the photothermal bi-reforming of methane (PT-BRM) using a reaction feed of CH₄(22.5 mL min⁻¹)/CO₂(12.0 mL min⁻¹)/H₂O(11.0 mL min⁻¹)/N₂(10.0 mL min⁻¹)/Ar(145 mL min⁻¹). In the PT-BRM test, the r_{H_2} increased significantly to over 100 mmol h⁻¹ compared to the PT-DRM results (Figure 4.8c). The CO₂ and CH₄ conversions were approximately 75% and 73%, respectively, after 52 h of the activity test. The H₂/CO ratio was 1.4 in PT-BRM conditions, substantially higher than that observed in PT-DRM. Furthermore, the amount of the deposited coke after 52 h was only 0.6 wt%, indicating a significant reduction of coke formation due to steam addition. These results suggest that combining the developed gap reactor with PT-BRM could pave the way for highly active and stable solar reforming systems. Additionally, this study underscores the critical role of reactor design in photothermal reactions and provides a novel method for developing efficient photo-reactors.

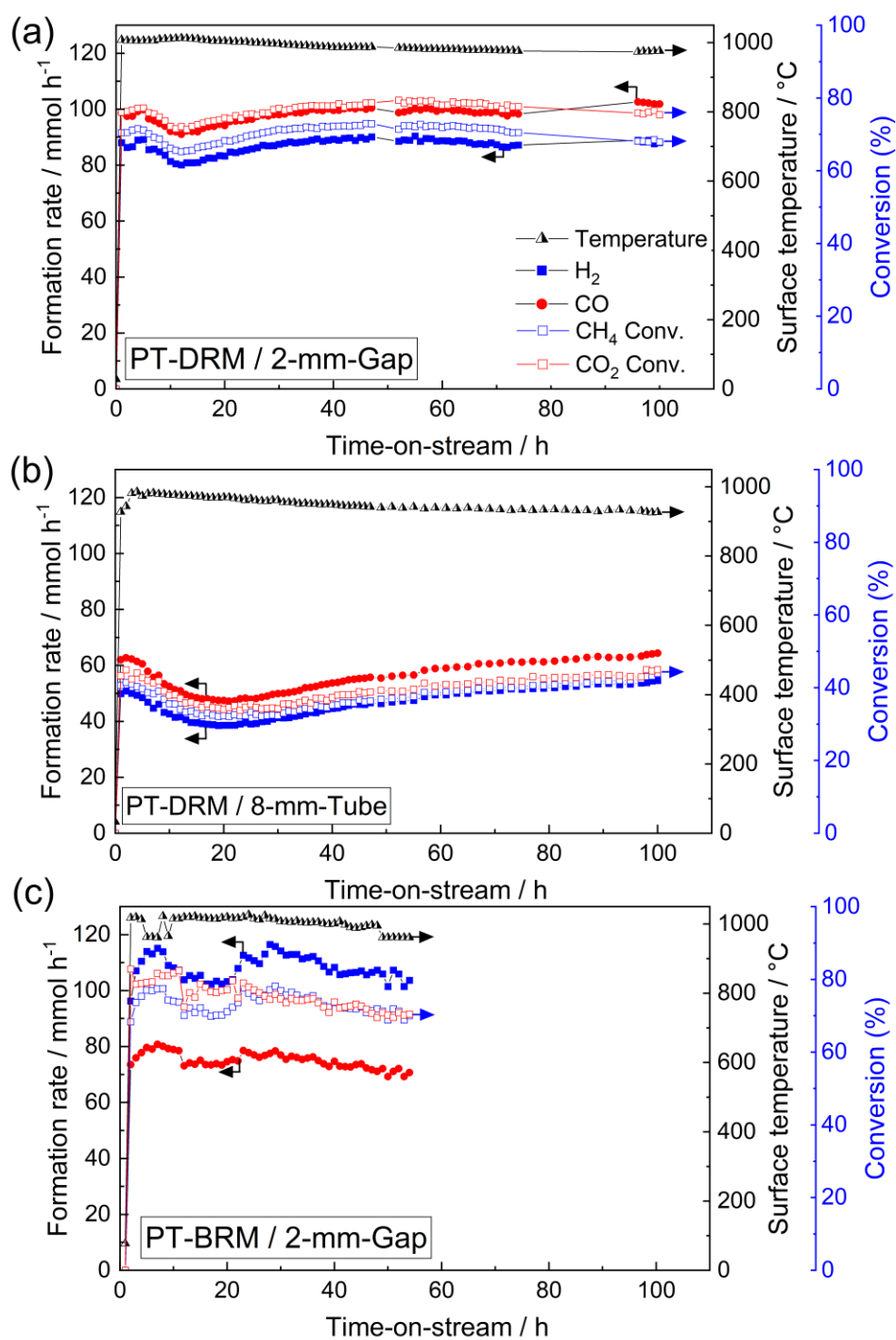


Figure 4.8 Results of the long-time stability test using various reactors. (a): 2-mm gap reactor in PT-DRM. (b): 8-mm tubular in PT-DRM. (c): 2-mm gap reactor in PT-BRM. ($P = 25$ W, $\Phi = 7$ mm, and spot position: middle).

Table 4.2 Selected results of light-driven dry reforming of methane without external heating.

Catalyst	Reactor type	Light source	Feed /l ^a mL min ⁻¹	Conversion (%)		Efficiency (%) ^b	Details of light conditions ^c	Ref. ^d
				CH ₄	CO ₂			
Co ₅ Ni ₉₅ @SiO ₂	Gap reactor,	Xe lamp,	$F_{\text{CH}_4} = 22.5$	72	78	$\eta = 6.0$	$P = 25 \text{ W}$ $\Phi = 7 \text{ mm}$ $I = 650 \text{ kW m}^{-2}$ $\lambda > 435 \text{ nm}$	This study
	Tube-based,	300 W	$F_{\text{CO}_2} = 22.5$					
Co ₅ Ni ₉₅ @SiO ₂	Tube-based reactor	Xe lamp, 300 W	$F_{\text{CH}_4} = 20$ $F_{\text{CO}_2} = 25$	40	41	$\eta = 6.5$	$P = 25 \text{ W}$ $\Phi = 7 \text{ mm}$ $I = 650 \text{ kW m}^{-2}$ $\lambda > 435 \text{ nm}$	[15]
25 wt% Ni/SiO ₂	Tube-based reactor	Xe lamp, 300 W	$F_{\text{CH}_4} = 20$ $F_{\text{CO}_2} = 25$	8.2	7.5	-	$P = 17.3 \text{ W}$ $\Phi = 20 \text{ mm}$ $I = 55 \text{ kW m}^{-2}$ $\lambda > 435 \text{ nm}$	[16]
1.2Ni-0.3Co/SiO ₂	flow type reactor	Xe lamp, 300 W	$F_{\text{CH}_4} = 9.6$ $F_{\text{CO}_2} = 9.6$	-	$n.d.^{[e]}$ (~23)	-	$I = 90 \text{ kW m}^{-2}$	[17]
Silica-cluster-modified Ni/SiO ₂	Stainless-steel cavity reactor	Xe lamp 500 W	$F_{\text{CH}_4} = (13.9)$ $F_{\text{CO}_2} = (13.7)$	$n.d.^{[e]}$ (~37)	$n.d.^{[e]}$ (~41)	$\eta = 12.5$	$P = 6.74 \text{ W}$ $\Phi = 5 \text{ mm}$ $I = 343.6 \text{ kW m}^{-2}$ Full spectrum	[32]

Rh/SrTiO ₃	Stainless- steel cavity reactor	Hg– Xe lamp, 150 W	$F_{\text{CH}_4} =$ (0.01) $F_{\text{CO}_2} =$ (0.01)	$n.d.^{[e]}$ (~28)	$n.d.^{[e]}$ (~28)	AQE = 5.9	Abs. photon number: 1.25×10^{17} (quanta cm $^{-2}$ s $^{-1}$)	[33]
NiCo/ MgO-Al ₂ O ₃ (Ni/Co = 1)	Stainless- steel cavity reactor	Xe lamp, 300 W	$F_{\text{CH}_4} =$ (44.4) $F_{\text{CO}_2} =$ (44.7)	$n.d.^{[e]}$ (~55)	$n.d.^{[e]}$ (~63)	$\eta =$ 33.8	$P = 12.6$ W $\Phi = 6$ mm $I = 445.6$ kW m $^{-2}$ Full spectrum (Xe)	[34]
NiCo@MgO/M gO (Ni/Co = 2)	Stainless- steel cavity reactor	Xe lamp, 500 W	$F_{\text{CH}_4} =$ 36 $F_{\text{CO}_2} =$ 36	$n.d.^{[e]}$ (~40)	$n.d.^{[e]}$ (~48)	$\eta =$ 39.3	$P = 7.8$ W $\Phi = 5$ mm $I = 396.8$ kW m $^{-2}$ Full spectrum	[35]
Pt/Co-Al ₂ O ₃	Stainless- steel cavity reactor	Xe lamp 500 W	$F_{\text{CH}_4} =$ (25.7) $F_{\text{CO}_2} =$ (25.8)	$n.d.^{[e]}$ (~35)	$n.d.^{[e]}$ (~43)	$\eta =$ 27.2	$P = 6.7$ W $\Phi = 5$ mm $I = 343.0$ kW m $^{-2}$ Full spectrum	[36]
Co/Mg-CoAl ₂ O ₄	Stainless- steel cavity reactor	Xe lamp 500 W	$F_{\text{CH}_4} =$ (27.2) $F_{\text{CO}_2} =$ (27.7)	$n.d.^{[e]}$ (~37)	$n.d.^{[e]}$ (~45)	$\eta =$ 34.2	$P = 6.3$ W $\Phi = 10$ mm $I = 80.5$ kW m $^{-2}$ Full spectrum	[37]

[a] F : flow rate of CO₂ or CH₄ (mL min⁻¹). [b] η : light-to-fuel conversion efficiency, AQE: apparent quantum efficiency as reported by the authors. [c] Conditions of light irradiation. P : power, Φ : light spot diameter, I : light intensity, and λ : wavelength of light. [d] Reference. [e] No data. The values in parentheses are calculated ones based on the values or Figures in the papers.

Conclusion

In photothermal dry-reforming of methane (PT-DRM), the temperature gradient induced by light irradiation poses a significant challenge, as catalysts at a low-temperature zone promote the reverse reaction, thereby reducing overall catalytic performance. This study demonstrated the effectiveness of a novel gap reactor with controllable thickness for mitigating a temperature gradient and enhancing catalytic performance in PT-DRM. Using the gap reactor, approximately 78% of CO₂ conversion and 72% of CH₄ conversion were achieved over 100 hours on the Co–Ni@SiO₂ catalyst developed by our group previously. Compared to the conventional tube reactors, the gap reactor exhibited substantially higher conversion and long-term stability. Furthermore, the developed gap reactor showed excellent catalytic performance for the photothermal bi-reforming of methane, with suppressed coke formation to only 0.6 wt% after approximately 50 hours of reaction. These findings highlight the potential of this novel gap reactor design for photothermal catalysis, offering a promising pathway for advancing catalytic reforming processes powered by solar energy.

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Chapter 5

General Conclusion

In this dissertation, the enhancement of photothermal methane (CH_4) reforming was thoroughly investigated using multiple approaches including catalyst development, optimization of reaction conditions, and advancements in reactor design. The author investigated photothermal dry reforming of methane (PT-DRM) and photothermal bi-reforming of methane (PT-BRM) since they have strong potential to mitigate CH_4 and CO_2 emissions. These two reactions have the merit of employing the solar energy to convert the greenhouse gases into valuable syngas (CO and H_2) feedstock. In addition, the author provided new insights into the differences between photothermal and thermally catalyzed CH_4 reforming reactions. A key distinction, as introduced in earlier chapters, lies in the unique temperature gradients induced by non-uniform light distribution in photothermal catalytic reactions. The author tried to evaluate the influence of this temperature gradient on the catalytic process and then dealt with it using two different strategies. The first strategy was to maximize the temperature gradient and tailor the catalytic reaction towards effective utilization. In the second strategy, the author aimed to suppress this temperature gradient.

In chapter two, the author focused on the catalytic materials and the irradiation conditions. To enhance the catalytic conversion and stability of Ni-based catalysts, the author integrated two techniques, i.e. alloying and preparing yolk-shell structures. The Co-Ni alloy catalysts with tiny amounts of Co (between 1-5 mol%) was found to strongly enhance the catalytic conversion as well as the catalyst stability compared to monometallic Ni and Co-rich catalysts. Then, the role of the yolk-shell catalyst structures was investigated by comparing them with counters prepared by impregnating the same alloy composition on commercial SiO_2 . As a result, the $\text{Co}_5\text{Ni}_{95}@\text{SiO}_2$ catalyst was the optimum since it persevered through the harsh reaction conditions with temperature gradient. For instance, the particle size distribution of the yolk $\text{Co}_5\text{Ni}_{95}$ alloy nanoparticles encapsulated by porous SiO_2 shell barely changed after the activity tests compared with the impregnated one. This highlighted the enhanced resistance against sintering under high reaction temperatures. Moreover, the coke deposition was substantially suppressed by using this

catalyst. This allowed the investigation of various irradiation conditions (power, spot size, and position) without the interference from the catalyst deactivation. This investigation provided valuable knowledge about the role of the temperature gradient on the photothermal CH₄ conversion.

In chapter three, the temperature gradient was utilized to promote tandem catalytic process. It was challenging to combine reactions of different operational temperatures in one system. However, the author utilized the temperature gradient, comprising high-temperature zone and low-temperature zone, to overcome this challenge to promote the combination of two reactions with different operational temperature ranges in one system.

In this chapter, the author elaborated the rationale sequence of temperature zones to accommodate the highly endothermic CH₄ reforming and the exothermic Fischer-Tropsch synthesis (FTS) reactions in series. This led to the direct conversion of the CH₄ and CO₂ into hydrocarbons in a single-pass system via the tandem CH₄ reforming-FTS process. In this study, the author investigated various relevant parameters that would enhance the formation rates of the syngas and C₂₊ hydrocarbons including: the catalyst loading, catalyst porosity, reaction conditions, and single- and dual-bed arrangements. The influence of each of these parameters on the formation rates of syngas and C₂₊ hydrocarbons was elaborated. For instance, the catalyst porosity was found to significantly affect the formation rates of these products. The author also clarified the effect of reaction conditions on the interrelations between the syngas formation and the hydrocarbons formation. The increase in syngas was found to increase the hydrocarbons. Catalysts that showed low syngas formation produced low or no C₂₊ hydrocarbons. For instance, the Co₅Ni₉₅@SiO₂ showed superior stability in the syngas and C₂₊ hydrocarbons formation rates. Meanwhile, the Ru₁₀₀@SiO₂ catalyst had high and stable syngas formation rates but the C₂₊ hydrocarbons formation rates were not stable and deteriorated with time. Strikingly, their olefin and paraffin selectivity varied remarkably between these two catalysts which underscores the potential of this process.

In chapter four, the author adopted another approach to deal with the temperature gradient from the viewpoint of the reactor design. In this strategy, the author tried to achieve high temperatures with narrow temperature distribution at the same time. To achieve these goals, it was necessary to: (a) determine the effect of irradiation flux on promoting the photothermal CH_4 reforming, and (b) expose the catalyst to as uniform light distribution as possible. Hence, a novel flow-type photo-reactor with a quartz filler was developed. The purpose was to control the catalyst amount and homogenize the catalyst bed thickness to match the light distribution.

In this chapter, several reactors which had quartz filler welded inside a quartz tube. The quartz filler had a beveled side that made gap space to accommodate the catalysts. By varying the gap thickness, the catalyst amounts changed, thereby changing the irradiation flux per catalyst mass. The author elaborated the influence of using the optimal gap thickness of the novel reactor design on increasing the photothermal CH_4 conversion to 80%. To clarify the advantage of this reactor, the author compared this gap reactor with conventional tubular reactors. Surprisingly, the gap reactors had two-fold increase in CH_4 conversion compared to the conventional tubular reactors. In addition, the activity tests using the gap reactors showed superior stability compared to the tubular counters in long time reaction for 100 h. This enhancement was due to the uniform light distribution that narrowed down the temperature gradient. The findings of this study enrich the understanding of the photothermal reactions and CH_4 reforming. This led to maximizing the syngas formation rates and minimized the backward methanation reaction. The author showed in this study that obtaining high photothermal CH_4 conversion was made possible by developing stable catalyst and using it with the improved reactor design.

In summary, this dissertation presents a comprehensive exploration of the potential for photothermal methane reforming to address critical challenges in energy conversion and greenhouse gases utilization. By integrating findings across catalyst development, reaction condition optimization, and reactor design, the author demonstrated the feasibility of achieving high photothermal CH_4 conversion. Beyond methane reforming, this work sets the stage for extending photothermal methodologies to tailor successive catalytic reactions.

Looking forward, there is plenty of room for future improvements. The findings of this dissertation pave the way for the implementation of the photothermal approach in energizing the CH_4 reforming reactions. To effectively benefit from the photothermal temperature gradient in

promoting the tandem catalytic processes, the author suggests future investigations. Although the fact that the formation rates of the syngas were much higher than that of C_{2+} hydrocarbons that were in micromole per hour order, several pathways for future enhancements are proposed. For instance, further development of multifunctional catalytic materials can increase the selectivity of the successive FTS reaction. For the reactor design, increasing the reaction pressure could further enhance the C_{2+} hydrocarbons yield and shift FTS product selectivity toward higher hydrocarbons, according to Le Chatelier's principle. Modifying the mass flow direction to align with the irradiation direction could improve light absorption within the catalyst bed, enhancing energy conversion efficiency. The reactor design can also be further enhanced to use cheaper materials and implement 3D catalyst structures.

The findings presented in this dissertation enrich the understanding of photothermal catalytic processes, offering valuable insights for future advancements. By addressing both fundamental and applied aspects, this work contributes to the growing field of photothermal catalysis and its role in developing energy-efficient and environmentally friendly technologies. The author hopes the work presented in this dissertation will help to comprehensively enhance the applicability of the photothermal driven reactions to better design catalytic systems for energy and materials resources.

Publication list

Chapter 2

Photothermal Dry Reforming of Methane on Yolk-Shell Co–Ni Alloy@SiO₂ catalyst

ChemCatChem, **2024**, e202401396.

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Chapter 3

Photothermal Tandem Catalysis of CH₄ Reforming and Fischer-Tropsch Synthesis to Produce Syngas and C₂+ Hydrocarbons.

Solar RRI, **2025**. DOI: 10.1002/solr.202500021.

Chapter 4

A Gap-designed Photo-reactor for High-Performance Photothermal Methane Reforming

Sustainable Energy & Fuels. **2025**. DOI: 10.1039/D4SE01830C.

Patent

リアクター及び気相反応方法” *Reactor and gas-phase reaction method for Photothermal Methane Reforming*. Japanese Patent No. 2024-192704, 2024.

