



Siqi Wang

Development of bimetallic catalysts for (sorption-enhanced) steam
methane reforming

School of Water, Energy and Environment
PhD in Energy and Sustainability

PhD
Academic Year: 2021 - 2024

Supervisor: Dr Peter T. Clough
Associate Supervisor: Dr Seyed Ali Nabavi
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the degree of PhD

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Abstract

Hydrogen has gained increasing attention in recent years as one of the most promising solutions to decarbonize the energy sector, as it emits zero carbon when combusted. The demand for clean hydrogen continues to rise as government, industry, and academia endeavour to meet the net zero goal by the year 2050. Steam methane reforming is currently the predominant hydrogen production pathway and is predicted to remain so for the years to come. Many techniques exist for the optimization and decarbonization of the steam methane reforming process. Two of the most widely employed methods include using more efficient and stable catalysts and adding in an in-situ carbon capture step using solid CO₂ sorbents. The overall aim of this PhD study is to develop and evaluate the performance of novel bimetallic catalysts for the (sorption-enhanced) steam methane reforming process. Starting from a comprehensive literature review, recent advances in the field of bimetallic SMR catalysts were summarized and reviewed, based on their catalytic activity, stability, and physical-chemical properties. Based on the review, three bimetallic catalysts (Ni₃M₁/Al₂O₃, M = Cu, Fe, and Ge) were synthesized, characterized using different techniques, and tested in a laboratory-scale fixed bed reactor under typical steam methane reforming conditions. CaO particles were then added to the system and the performance of the catalysts under sorption-enhanced steam methane reforming conditions was evaluated. A study on the influence of Cu loading on the bimetallic Ni-Cu catalysts was also carried out. The experimental studies were also accompanied by Density Functional Theory calculations of the carbon and oxygen adsorption energies on the bimetallic surfaces, and microkinetic modelling of the SMR reaction based on previous literature on its reaction mechanism. Finally, machine learning models were developed for the prediction of atomic adsorption energies using readily available elemental properties. Together with the previously developed microkinetic model, a fast high throughput screening of bimetallic alloys was carried out and catalysts with high sulphur resistance were successfully identified. Overall, the addition of Cu was found to be highly beneficial for promoting the catalytic activity of the conventional Ni catalysts, and the addition of Ge promotes the activity and can potentially

improve the sulphur resistance of the catalysts. The wide application of these cost-effective and highly active bimetallic catalysts will contribute significantly to the decarbonisation of the energy sector by enabling the efficient production of hydrogen.

Keywords:

Hydrogen production, Density Functional Theory, Microkinetic Modelling, Machine Learning, Sulphur resistant catalysts, Materials.

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List of Abbreviations

ANN	Artificial Neural Network
at. %	Atomic percentage
BEP	Brønsted–Evans–Polanyi
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CAPEX	Capital expenditure
CCUS	Carbon capture, utilization, and storage
CL-SMR	Chemical looping steam methane reforming
CSCM	Combined Sorbent Catalyst Materials
CV	Cross-validation
DFT	Density Functional Theory
EDX	Energy dispersive X-ray
ETR	Extra Trees Regression
GBR	Gradient Boosting Regression
GGA	Generalized gradient approximation
GHSV	Gas hourly space velocity
KNN	K-Nearest Neighbours Regression
Light GBM	Light Gradient Boosting Machine
MAE	Mean Absolute Error
MKM	Microkinetic modelling or Microkinetic model
ML	Machine Learning
Mol. %	Molar percentage
MSE	Mean Squared Error
OPEX	Operating expense
PAW	Projection augmented wave
PBE	Perdew–Burke–Ernzerhof
RFE	Recursive Feature Elimination
RFR	Random Forest Regression
RR	Ridge Regression
SEM	Scanning electron microscopy
SESMR	Sorption-enhanced steam methane reforming
SMR	Steam methane reforming

SVR	Support Vector Regression
TGA	Thermogravimetric analysis
TOF	Turnover frequency
TRL	Technology Readiness Level
UBI-QEP	Unity bond index-quadratic exponential potential
vol.%	Volume percentage
WGS	Water-gas shift reaction
wt.%	Weight percentage
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence analysis
YSZ	Yttria-stabilized zirconia

1 Introduction

1.1 Background

Since the pre-industrial period, human activities have increased Earth's global average temperature by approximately 1 °C [1]. The majority of the increase took place since 1975, with an average rate of 0.15 – 0.2 °C per decade [2]. Some of the consequences of global warming include drought, fires, rising sea levels, and water scarcity, which can severely impact people's living conditions, especially those living in island nations or developing countries. In light of this situation, a growing coalition of countries is committing to net zero emissions by 2050. To achieve its net zero target by 2050, the UK Government has set out a series of measures to reduce emissions across the economy and support transitions to a low-carbon future. This includes creating or integrating carbon capture and storage (CCUS) units into current facilities, employing greenhouse gas removal techniques, or switching to low-carbon or renewable energies for fuel and power supply [3]. For the latter approach, the UK Government's Hydrogen Strategy [4] recognized the important role that hydrogen plays in achieving the net zero goal. Based on their estimation, a total of 7 – 20 GW of hydrogen production capacity is needed in 2035 and 15 – 60 GW in 2050. This requires a significant amount of research and development in the field of hydrogen production, transportation, utilization, and storage.

Hydrogen is extensively used by industry for petroleum refining, metal treating, fertilizer production, and food processing, or as a rocket fuel. Currently, hydrogen is mainly produced using fossil fuels (e.g. coal and natural gas) and therefore accounts for a significant proportion of global carbon emissions. However, as mentioned previously, hydrogen and hydrogen-based fuels can potentially play a very important role in sectors that are difficult to decarbonize – including heavy industry or long-distance transportation, where alternative solutions are unavailable or difficult to implement [5]. This demands the utilization of clean hydrogen produced from renewable or nuclear energy, or fossil fuel with carbon capture techniques in place.

The production of low-carbon hydrogen can be divided into five categories (Figure 1-1, extracted from [8]):

- Biological routes: which include the use of microorganisms to convert biomass to hydrogen and other end products through anaerobic digestion, photolysis, fermentation, and microbial electrolysis [6]. By-products from the process can also add value to the overall system.
- Electrolytic routes: which include using electrolyzers to split water into hydrogen and oxygen. Although commercial electrolyzers have been in use for years, research is still needed to explore new options such as anion and proton exchange membrane electrolysis [7].
- Solar to fuels routes: which include water splitting using solar energy, and solar energy-based thermochemical and photobiological technologies [8].
- Thermochemical routes: which typically involve using heat and fossil fuels for the large-scale production of hydrogen. One of the most important thermochemical techniques is steam methane reforming (SMR), which is also the subject of this research. Alternative thermochemical techniques include autothermal reforming, partial oxidation, gasification, and microwave-related technologies. These techniques are usually coupled with CCUS units to mitigate the CO₂ emissions originating from the fossil fuel-based feedstock.

Potential components of the low-carbon hydrogen system

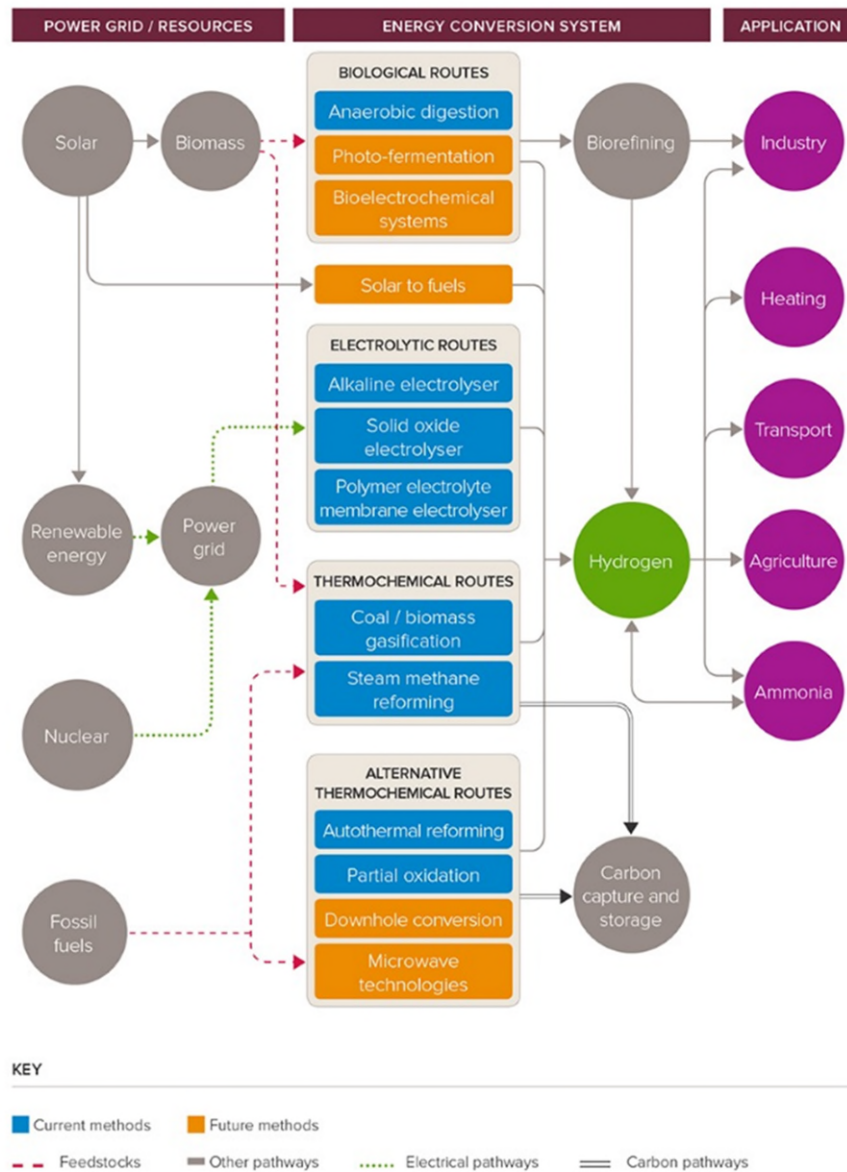


Figure 1-1 Components of the low-carbon hydrogen production system.

SMR is the predominant technology used for the production of bulk hydrogen, which accounts for approximately 50% of the global hydrogen generation. However, for every kg of hydrogen produced by SMR, 8 – 12 kg of CO₂ is emitted. Retrofitting or coupling SMR with carbon capture is one of the options to reduce its emissions [9]. Among these technologies, one of the most promising ones for cost-effective low-carbon hydrogen production is sorption-enhanced steam

methane reforming (SESMR), where an in-situ CO₂ capture step takes place simultaneously with the conventional SMR process [10]. A recent project led by Cranfield University, “HyPER”, aims to provide a pilot-scale demonstration of SESMR, and take this novel technology from Technology Readiness Level (TRL) 4 to 6 [11]. Compared with commercialised process with tail-end carbon capture units, the advantages of the proposed system include a ~20% reduction in the levelized cost of hydrogen with a 50% reduction in Capital Expenditure (CAPEX) and Operating Expenses (OPEX), while maintaining a CO₂ capture efficiency of over 95%. The SMR reaction requires the presence of a catalyst to proceed. Although Ni-based catalysts (usually supported by alumina or silica) have been extensively used for commercial SMR processes, some aspects of the materials still require further optimization. It is therefore of interest to study the performance of novel bimetallic SMR catalysts under SMR and SESMR conditions.

Generally speaking, a catalyst is evaluated based on its activity, selectivity, and stability. In the case of (SE)SMR, the activity and selectivity of a given catalyst are usually assessed based on its methane conversion rate, hydrogen selectivity, and CO selectivity [12]. The stability of a catalyst can be examined from different perspectives, including its long-term activity, resistance to poisoning, and sintering. Extensive research has been carried out to evaluate and improve the long-term stability, carbon resistance, and sintering resistance abilities of bimetallic catalysts [13–15]. However, there is a lack of literature regarding the sulphur-resistant ability of bimetallic catalysts. Existing studies mainly rely on the “trial and error” approach in search of suitable sulphur-resistant catalysts for SMR [16–19]. The need for highly active sulphur-resistant catalysts is, however, urgent to industrial-scale SMR processes, as the presence of sulphur-containing impurities in natural gas streams is usually inevitable and expensive to eliminate [20]. It is therefore essential to adopt a systematic approach for screening and selecting catalysts that demonstrate resilience against sulphur, thereby meeting the demand for reliable performance in industrial applications.

The main aim of this PhD study is therefore to develop novel catalysts and investigate their performance under SMR and SESMR conditions, with a focus

on their catalytic activity and stability. Starting with a comprehensive literature review of recent research, the advantages and limitations of using bi/polymetallic materials as catalysts were thoroughly studied. Several promising candidates were then selected based on conclusions from the review and the materials were synthesized. The performance evaluation process includes the testing of the catalysts in a laboratory-scale fixed bed reactor, with a focus on their catalytic activity and coke-resistant ability. The experimental testing was followed by first-principle Density Functional Theory (DFT) calculations and Microkinetic Modelling (MKM). Finally, by harnessing the power of Machine Learning (ML), the sulphur-resistant ability of over 500+ bimetallic materials was evaluated numerically. Findings from this study provide insights into the application of bimetallic catalysts for the production of low-carbon hydrogen and point out the directions for future research in this area.

1.2 Aim and objectives

This research aims to investigate the performance of novel bimetallic catalysts for the production of hydrogen via SMR and SESMR. The following objectives were addressed in order to deliver against the overall aim:

1. Assess the performance of conventional SMR catalysts and identify potential bimetallic materials with high catalytic activity and stability under SMR conditions.
2. Synthesize and characterize a conventional monometallic Ni/Al₂O₃ catalyst and three Ni-based bimetallic catalysts (Ni₃Cu₁/Al₂O₃, Ni₃Fe₁/Al₂O₃, and Ni₃Ge₁/Al₂O₃), and test their performance under SMR and SESMR conditions.
3. Investigate the effect of Cu loading on the performance of bimetallic Ni-Cu/Al₂O₃ catalysts for SMR and SESMR.
4. Screen bimetallic material databases for sulphur-resistant SMR catalysts, based on atomic adsorption energies predicted by ML models and results from DFT calculations and microkinetic modelling.

1.3 Novelty

The intellectual contribution of this work and the knowledge gaps that this research aims to address are outlined as follows:

- Recent studies on bi/polymetallic catalysts were summarised and critically reviewed. The advantages and limitations of using bi/polymetallic catalysts were analysed and several promising materials were selected for further evaluation.
- Three Ni-based bimetallic catalysts (Ni/Al₂O₃ promoted by Cu, Fe, and Ge) were tested for the first time for both conventional SMR and the novel SESMR process. To the best of the author's knowledge, this was also the first-ever attempt to apply germanium-based catalysts for the reforming process. The atomic adsorption energies of carbon and oxygen on these catalysts were obtained using DFT calculations and evaluated against results from a microkinetic model.
- The effect of Cu loading on the performance of the bimetallic Ni-Cu catalysts under SMR and SESMR conditions was investigated. The influence of Cu concentration on the carbon and oxygen adsorptive ability was also studied using DFT.
- A systematic screening of sulphur-resistant SMR catalysts was carried out for the first time. ML models were developed to predict the atomic adsorption energies on bimetallic surfaces with different Metal₁:Metal₂ ratios. Combined with results from the microkinetic model, over 500 bimetallic materials were screened, and 49 were identified as highly active SMR catalysts, among which 10 were identified as sulphur resistant.

1.4 Thesis outline

The structure of this research and the linkage between each section is illustrated in Figure 1-2. The outline of the thesis is described as follows:

Chapter 1: This chapter presents the background and motivation for this research, the aim and objectives of this work, the knowledge gaps this research aims to fill, and a summary of the thesis.

Chapter 2: This chapter addresses Objective 1. In this chapter, a critical review of recent studies on bi/polymetallic catalysts for SMR and SESMR was carried out. The main focus of this chapter was on Ni-based catalysts promoted by noble metals, non-noble metals, and metalloids. However, other transition metal-based bimetallic catalysts and polymetallic catalysts were also considered to ensure that a comprehensive list of literature is included. Results from both experimental testing and numerical simulations were included in this chapter, and directions for future research were suggested at the end of this chapter.

Chapter 3: This chapter addresses Objective 2. Three bimetallic catalysts with potentially high SMR activity were selected based on the literature review. The catalysts were characterized using various techniques and tested under both SMR and SESMR conditions. The experimental results were further confirmed by DFT calculations of relevant adsorption energies and a MKM of the SMR reaction. The bimetallic catalysts were also compared with the baseline scenario – a conventional monometallic Ni/Al₂O₃ catalyst.

Chapter 4: This chapter addresses Objective 3 and is linked to Chapter 3. One of the bimetallic catalysts (Ni-Cu/Al₂O₃) was further investigated, and the effect of Cu loading in the bimetallic materials was studied. Similar to the previous chapter, the catalysts were tested under SMR and SESMR conditions and the results were evaluated against numerical models.

Chapter 5: This chapter addresses Objective 4. A database containing atomic adsorption energies on common transition metal- and metalloid-based surfaces was built with DFT-calculated data. Different ML algorithms were used and evaluated for the fast prediction of adsorption energies on mono and bimetallic surfaces. Combining ML-predicted adsorption energies and the MKM developed in Chapter 3, a high throughput screening of sulphur-resistant bimetallic catalysts was carried out and several materials were identified as promising candidates.

Chapter 6: This final chapter provides a summary of the thesis and presents the intellectual contributions of the key findings, as well as recommendations for future research.

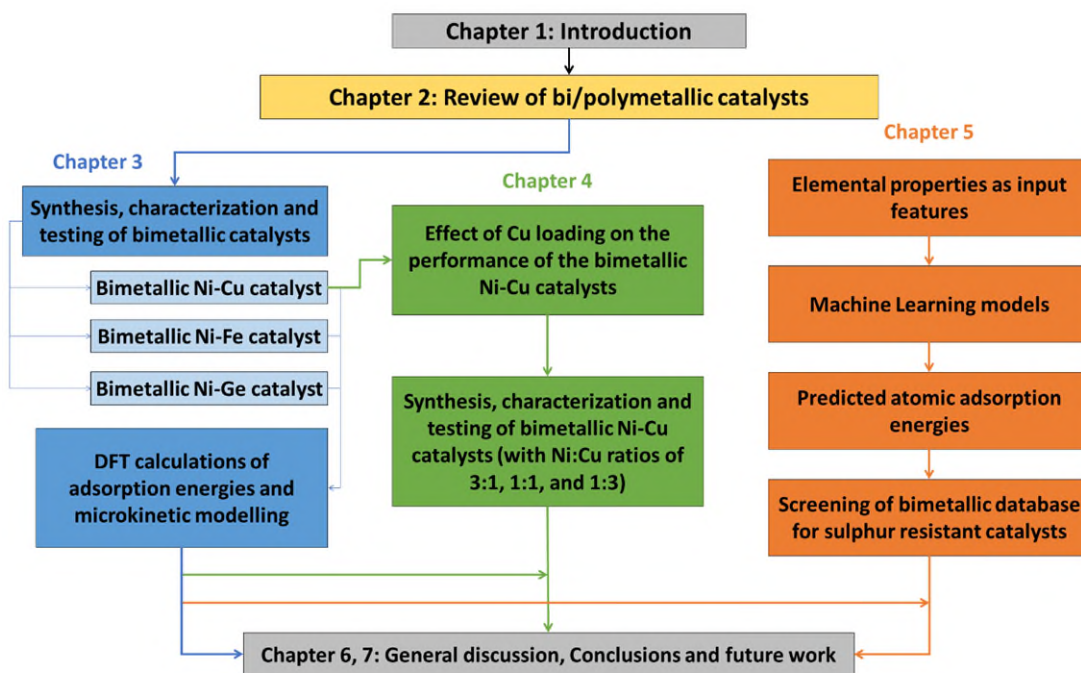


Figure 1-2 Structure of the thesis and linkage between each work package.

1.5 List of published/submitted work

Published papers and the chapters in which they are presented in this thesis are as follows:

1. Siqi Wang, Seyed Ali Nabavi, Peter T. Clough, A review on bi/polymetallic catalysts for steam methane reforming. *Int J Hydrogen Energy* 2023;48:15879–93. <https://doi.org/10.1016/j.ijhydene.2023.01.034>. (Chapter 2)
2. Siqi Wang, Ziqi Shen, Amin Osatiashtiani, Seyed Ali Nabavi, Peter T. Clough, Ni-based bimetallic catalysts for hydrogen production via (sorption-enhanced) steam methane reforming, *Chemical Engineering Journal*, Volume 486, 2024, 150170, ISSN 1385-8947, <https://doi.org/10.1016/j.cej.2024.150170>. (Chapter 3)
3. Siqi Wang, Satya S. K. Kasarapu, Peter T. Clough, High-Throughput Screening of Sulfur-Resistant Catalysts for Steam Methane Reforming Using Machine Learning and Microkinetic Modeling, *ACS Omega*, <https://doi.org/10.1021/acsomega.4c00119>. (Chapter 5)

Manuscript under review and the chapter in which it is presented in this thesis are as follows:

1. Wang S, Shen Z, Osatiashtiani A, Nabavi SA, Clough PT. Experimental and DFT study of steam methane reforming over bimetallic Ni-Cu catalysts. Submitted to Fuel, currently under review (April 2024). (**Chapter 4**).

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2 A review on bi/polymetallic catalysts for steam methane reforming

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Abstract

Blue hydrogen production by steam methane reforming (SMR) with carbon capture is by far the most commercialised production method, and with the addition of a simultaneous in-situ CO₂ adsorption process, sorption-enhanced steam methane reforming (SESMR) can further decrease the cost of H₂ production. Ni-based catalysts have been extensively used for SMR because of their excellent activity and relatively low price, but carbon deposition, sulphation, and sintering can lead to catalyst deactivation. One effective solution is to introduce additional metal element(s) to improve the overall performance. This review summarizes recent developments on bi/polymetallic catalysts for SMR, including promoted nickel-based catalysts and other transition metal-based bi/polymetallic materials. The review mainly focuses on experimental studies, but also includes results from simulations to evaluate the synergistic effects of selected metals from an atomic point of view. An outlook is provided for the future development of bi/polymetallic SMR catalysts.

Keywords:

Metallic catalysts, Alloy, Steam methane reforming, Sorption-enhanced steam methane reforming, Hydrogen production, Syngas

2.1 Introduction

In recent years, hydrogen has gained increasing attention as an alternative to fossil fuels, enabling net zero targets to be realized. As stated in the 2021 UK Hydrogen Strategy [1], the UK is aiming for a total of 10 GW of low-carbon hydrogen production capacity by 2030 to decarbonize vital industries and provide clean energy across the heat, power, and transport sectors. This requires considerable effort in scaling up and optimizing carbon

capture and storage systems as well as new hydrogen production processes, such as sorption-enhanced reforming.

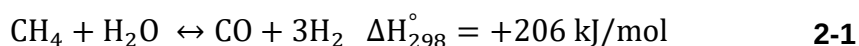
Hydrogen can be produced from a variety of renewable and non-renewable sources, and can be divided into three categories depending on its production pathway:

- Black/Grey/Brown hydrogen: from fossil fuel-based production (coal, natural gas, and lignite, respectively) with CO₂ released to the atmosphere.
- Blue hydrogen: from fossil fuel-based production with carbon capture, utilization, and storage (CCUS).
- Green hydrogen: from renewable sources, commonly electrolysis-based production.

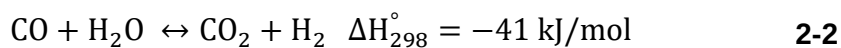
Different hydrogen production pathways using renewable sources have been investigated, including water electrolysis [2], thermochemical (pyrolysis and gasification), or biological conversion (fermentation and photolysis) of biomass [3]. However, various techno-economic studies have demonstrated that compared to these processes, fossil fuel reforming with CCUS remains the most cost-competitive option with the highest hydrogen production efficiency [4–6]. Steam reforming, partial oxidation, and autothermal reforming are three main fossil fuel reforming technologies for hydrogen production, among which the steam reforming of methane (SMR) is by far the most deployed method. Although SMR is a mature technology, one of the most significant problems is its high CO₂ emission. It is estimated that without CCUS, hydrogen from SMR has an emission factor of 222 – 325 g CO_{2eq} per kWh of H₂ (10 tCO₂/tH₂) [4,7].

Apart from the traditional approach of employing a downstream amine scrubbing process, an alternative option to mitigate carbon emissions is adding a simultaneous carbon capture step to the conventional SMR process. A novel hydrogen production technology, known as sorption-enhanced steam methane reforming (SESMR), combines the conventional SMR process with a simultaneous in-situ absorption of CO₂ using a solid sorbent (usually CaO). The main reactions involved in the SESMR process are as follows [8]:

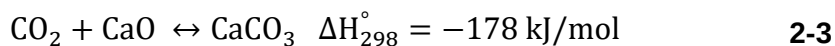
1. Steam reforming of methane



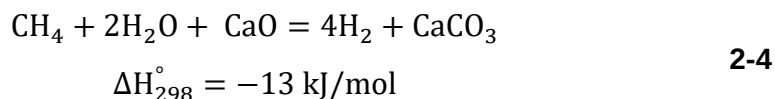
2. Water-gas shift (WGS) reaction



3. CO₂ sorption and sorbent regeneration



4. Overall equation for SESMR



In comparison to the traditional SMR process, SESMR enables the removal of CO₂ from the reaction zone, which shifts the equilibrium towards the product side, enhancing the production of hydrogen. The high-purity CO₂ stream released from the sorbent regeneration step can also be easily separated from the sorbent, and transported or stored for further use. The sorption-enhanced steam reforming process has been applied to other feedstocks as well, including phenol [9], glycerol [10], ethanol [11], and biomass [12]. In general, the CO₂ sorbent is combined with active catalytic metal(s) to form a bi-functional material, using alumina, perovskite, or mayenite as the structural support. Since both SMR and SESMR require the use of catalysts to proceed, and the types of catalysts used for both processes are in general identical, they will be reviewed holistically in this paper.

The main reaction steps of SMR are listed in Table 2-1, including the dissociative adsorption of the reactants, dehydrogenation, and bond reformation steps. It is generally agreed that the activation of the first C-H bond of the CH₄ decomposition step (step 1) is the rate-determining step of SMR [13–15]; but at lower temperatures (T < 500 °C), the CO formation step (step 7) becomes dominant [14]. The energy barrier for C-H bond activation over the Ni surface is relatively low, and at the same time, the adsorption of C*, H*, and O* is not so strong that the species cannot react off the surface easily. Nickel is also widely employed commercially due to its low price and high availability. However, Ni-based catalysts are prone to sintering and coke formation [16,17], hydrogen reduction of nickel-based catalysts before the reforming process is also necessary for activating the material. It is, therefore, of interest to investigate the anti-sintering ability and coke resistance, as well as the reducibility and self-activation ability of SMR catalysts.

Table 2-1 Main reaction pathway of SMR.

Reaction step	No.
$\text{CH}_4(\text{g}) + 2^* \leftrightarrow \text{CH}_3^* + \text{H}^*$	1
$\text{H}_2\text{O} + 2^* \leftrightarrow \text{OH}^* + \text{H}^*$	2
$\text{OH}^* + 1^* \leftrightarrow \text{O}^* + \text{H}^*$	3
$\text{CH}_3^* + 1^* \leftrightarrow \text{CH}_2^* + \text{H}^*$	4
$\text{CH}_2^* + 1^* \leftrightarrow \text{CH}^* + \text{H}^*$	5
$\text{CH}^* + 1^* \leftrightarrow \text{C}^* + \text{H}^*$	6
$\text{C}^* + \text{O}^* \leftrightarrow \text{CO}^* + 1^*$	7
$2\text{H}^* \leftrightarrow \text{H}_2(\text{g}) + 2^*$	8
$\text{CO}^* \leftrightarrow \text{CO}(\text{g}) + 1^*$	9

Apart from nickel, noble metals (Rh, Ru, Pd, Pt, and Ir) are also promising candidates for SMR because of their excellent catalytic ability and resistance to carbon formation. Currently, there is no definitive conclusion as to how the noble metals are ordered regarding their catalytic activity for SMR, however, several experimental [18,19] and numerical [20,21] studies reported that the catalytic activity of noble metals follows the order of Rh ~ Ru > Ir > Pt ~ Pd. Despite their advantages, noble metal-based catalysts are limited by their high prices.

One way to maintain the excellent performances of noble metals while maintaining a reasonable price is by combining two or more types of metals, using cheap transition metals (usually nickel or cobalt) as the base and noble metals as promoters. Bi/polymetallic catalysts have gained increasing attention in recent years, and the synergistic effect between commonly used metal elements has been investigated experimentally and numerically. Numerical studies focus on the reaction pathway, activation energies of certain reaction steps (in particular the C-H bond cleavage of the CH₄ decomposition step), as well as the adsorption energies of atomic or molecular species on the catalyst's surface, which are indicators of the material's catalytic activity and stability. Some materials were also tested experimentally, usually in lab-scale reactors, and evaluated based on their methane conversion ability, hydrogen yield, etc. To the best of the author's knowledge, there has been no literature that systematically summarizes the bi/polymetallic catalysts that have

been employed in (SE)SMR. The aim of this review is therefore to provide an overview of the bi/polymetallic catalysts that have been tested for (SE)SMR, to summarize their advantages and limitations, and to identify the gap in current (SE)SMR catalyst development for future studies.

2.2 Nickel-based bimetallic catalysts

2.2.1 Ni-based catalysts promoted by noble metals

Amongst the eight noble metals, platinum group metals (including Rh, Ru, Ir, Pt, and Pd) have the highest SMR activity and are most commonly used as promoters for Ni-based catalysts. Their catalytic performance arises from the partially filled *d*-subshells – electrons can be easily added to or removed from these orbitals, resulting in an optimal interaction between the metal surface and the gas-phase adsorbate. A lower degree of *d*-band filling leads to the too-strong adsorption of both reactants and reaction products on the metal surface, which easily blocks the active catalytic surface. On the other hand, with a higher degree of filling, the metal surface does not interact strongly enough with the reactants, which is the case for both Ag and Au. This results in a relatively low catalytic activity but a more stable and clean metal surface, which is why Ag and Au are usually added for their coke-resistant property. There is currently no literature available regarding the use of Os as an SMR catalyst, possibly due to its tendency to form a volatile and toxic oxide – OsO₄ [18].

Ru-Ni catalysts have been tested under lab-scale experimental SMR conditions by Jeong et al. [22] to study the effect of doping Ru over Ni/Al₂O₃ and Ni/MgAl₂O₄. They concluded that adding a small amount of Ru (0.5 wt.%) greatly suppressed coke formation on the catalyst surface and facilitated NiO reduction. The coke-resisting ability of Ru was studied on an atomic scale using Density Functional Theory (DFT) [23]. It was demonstrated that when the noble metal was added, the activation energy of the CHO*-producing step (step 5 shown in Figure 2-1) was significantly lower than that of the C*- and H*-producing steps (step 4), meaning CO production was favoured over carbon deposition.

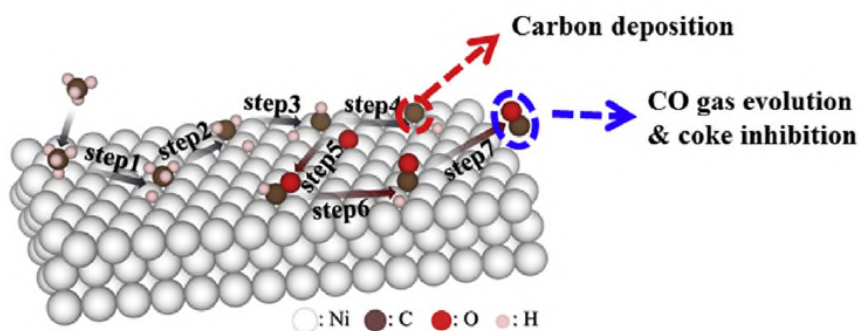


Figure 2-1 Reaction mechanism on Ni(111) and Ni-Rh / Ni-Ru (111) systems. Reprinted from [23] with permission from Elsevier.

Results also showed that Ru-promoted Ni catalysts were able to self-activate at a temperature of 700 °C without any pre-reduction using hydrogen, which is beneficial from an economic and process operation point of view [24,25]. Ni-based catalysts doped with small (0.5 wt.%) or even trace amounts (0.05 wt.%) of Ru showed good self-activation properties without pre-reduction, and achieved a higher CH₄ conversion rate compared to monometallic Ru or Ni catalyst. Ru decreased the reduction temperature of Ni by inducing hydrogen spillover on the Ni surface, a process in which H₂ molecules disassociate on the noble metal surface to H species and diffuse into Ni via the catalyst support.

Similar to Ru, the addition of Rh was also found to facilitate Ni reduction and produce a synergistic effect [26,27]. The bimetallic catalyst (with 0.2 wt.% Rh) showed higher activity compared to the linear combination of monometallic Rh or Ni catalyst. This was attributed to the enhanced textural properties of the bimetallic catalysts – the exposed metallic surface area and metal dispersion of the bimetallic catalysts, measured by CO chemisorption, was greatly promoted by the addition of Rh, and the increase was more significant with a higher Rh loading. The same synergistic effect was observed by Morales-Cano et al. as well [28], who studied the promoting effect of Ru, Rh, and Ir on Ni/ α -Al₂O₃ catalyst. The catalysts were also aged for 240 h at 800 °C with an S/C ratio of 6 to induce the sintering of Ni particles. The activity of the aged Ni-Rh and Ni-Ir was found to be significantly higher than the aged monometallic catalysts, proving their ability to resist Ni sintering. This ability was attributed to the migration and diffusion of Ni into the Face Centred Cubic structure of Rh and Ir during the aging process, which enabled the formation of Ni-Rh and Ni-Ir alloys, and retained the high surface area of the materials.

The optimal loading of noble metals in Ni-based catalysts was also investigated. Katheria et al. [29] tested a series of Ni/MgAl₂O₄ catalysts with Rh concentration varying from 0.1 to 1 wt.%. Results showed that 0.1 wt.% of Rh was sufficient to increase CH₄ conversion by

20%, whereas a further increase in Rh concentration did not have a significant effect. A higher metal loading does not necessarily mean a better catalytic ability due to the less-even distribution of active metal in the support. This observation was also verified by testing a series of Ni/MgAl₂O₄ catalysts with Pt loading varying from 0.01 to 1 wt.% [30,31]. Both studies reported that a Pt loading of 0.1 wt.% resulted in the highest catalytic activity. Further increase in Pt loading led to a decrease in both catalytic activity and stability. Results from the physical characterization of the materials showed that the highest surface area and maximum dispersion of active metal were achieved with 0.1 wt.% Pt loading, whereas higher Pt concentration, resulted in agglomeration on the material surface.

Chaichi et al. [32] synthesized a novel supportless Ni-Pd-carbon nanotube material and compared its performance with Ni and Ni-Pd catalysts under SMR conditions. The addition of Pd facilitated the reduction of metallic oxides, whereas both Pd and carbon nanotube increased the specific surface area. The resultant CH₄ conversion of the Ni-Pd-carbon nanotube material was 22% higher than the monometallic Ni/MgO catalyst. Reducibility enhancement by Pd was also reported by Batebi et al. [33] in a test of Ni-Pd/Al₂O₃ for combined steam and CO₂ reforming of methane. By adding Pd, the reduction degree was increased from 69% to 83%, leading to higher CH₄ conversion and H₂ yield while reducing coke deposition. Bimetallic Ni-Pd materials have also been tested for the oxidative SMR process [34–38]. Results from these studies demonstrated that the addition of Pd promoted the reduction of Ni, Pd-Ni alloy was also found to form preferentially on the material surface, contributing to its high activity and coke resistance.

Li and Miyata conducted a series of tests to study the doping effect of Ru [39,40], Rh [41,42], Pt [42–44], and Pd [42] on Ni/Mg(Al)O catalysts in a daily start-up and shut-down operation of SMR under steam purging. As was presented previously, the addition of all four types of promoters improved the reducibility of the catalyst by decreasing Ni reduction temperature and increasing the amount of hydrogen uptake on Ni. Ru, Rh, and Pt were also capable of suppressing the deactivation of the catalyst due to Ni oxidation, which was attributed to the self-regeneration of Ni⁰ from Ni²⁺ assisted by hydrogen spillover on the noble metal surface and the reversible reduction-oxidation between Ni⁰ and Ni²⁺ in the Mg(Ni, Al)O periclase. Self-activation without any reduction treatment of Rh-, Pt-, and Pd-Ni bimetallic catalysts was also observed during the daily start-up and shut-down operation. Compared to the complete deactivation of the pure Ni catalyst after the first steam purging, the CH₄ conversion of the bimetallic catalysts was kept at the value of thermodynamic equilibrium even after 4 cycles of steam purging. The self-activation and self-regeneration properties of

these bimetallic materials proved Ru, Rh, Pt, and Pd to be useful additives to the conventional Ni-based catalysts.

Although the reactivity of monometallic Ag and Au is relatively low, they have also been tested as promoters for Ni-based SMR catalysts due to their excellent stability. DFT-based studies [45,46] showed that the Ag-doped Ni surface is less prone to carbon deposition – the threefold Ag-Ni-Ni adsorption site is unstable for carbon atoms. Carbon atoms initially positioned at these sites will therefore move to the adjacent Ni-Ni-Ni site, which has lower adsorption energy. These negative interactions between the carbon atom and the Ag-Ni alloy surface indicate that Ag can be added as a coke-resistant promoter, which was also validated against experimental findings [47–49]. Both research teams studied the promoting effect of Ag (0.03 – 1 wt.%) on Ni/ γ -Al₂O₃ and concluded that even the minimum Ag loading of 0.3 wt.% could reduce carbon deposition significantly. However, this also compromised the catalytic activity of the material, which decreased by 25% compared to monometallic Ni catalysts. This is due to the fact that Ag atoms are energetically favoured to replace Ni atoms on the step edges, which are the most active sites for methane decomposition, compared to the terrace sites [50]. Similar properties were found in Au-doped Ni catalysts. Both computational [51–53] and experimental [54,55] studies suggested that the overall catalytic activity of Au-Ni was affected by the higher energy barrier for C-H bond cleavage in the rate-determining CH₄ dissociation step, whereas the stability of the material was enhanced due to the suppression of carbon formation.

Ag and Au have also been employed as promoters to Ni electrodes for solid oxide fuel cells under internal SMR conditions. Ag [56] or Au [57] with a loading of 1 – 5 wt.% doped on Ni/yttria-stabilized zirconia (YSZ), as well as Au with a loading of 1 – 4 at.% doped on Ni/CeO₂-Gd₂O₃ [58] anode was tested at temperatures ranging from 650 to 800 °C. Both exhibited satisfying performance with enhanced tolerance to carbon formation. However, the performance of Ag-doped materials is largely influenced by the reaction temperature. At temperatures higher than 750 °C, the Ag-Ni/YSZ cell degraded rapidly due to the low melting point of Ag [56]. At temperatures lower than 600 °C, the catalytic activity of the Ag-Ni/Al₂O₃ catalyst decreased significantly, whereas the Au-doped catalyst still exhibited higher activity than monometallic Ni/Al₂O₃ [59,60]. Sapountzi et al. [61] reported that an Au amount of 2.3 wt.% promoted the reducibility of Ni catalyst, and the Ni-Au alloy formed on the catalyst surface was able to inhibit the formation of sulphuric compounds, including nickel sulphide.

Liu et al. [62] reported that Ni-Ir alloy supported on MgAl₂O₄ was a durable catalyst for steam and CO₂ bi-reforming of methane under pressurized conditions. The bimetallic catalyst was

composed of small metallic clusters (with a mean size of ~ 2 nm) and the cluster size was retained for a duration of 434 h, in contrast to the significant increase in cluster size of the monometallic Ni/MgAl₂O₄ catalyst, showing the anti-sintering ability of Ir. The coke resistance of the bimetallic material was attributed to the combined effect of small ensemble sizes, increased surface oxophilicity, and higher activation barrier for CH₄ dissociation. The number of active sites was evaluated by H₂ chemisorption, it was found that an Ir loading of 0.1 wt.% was able to quadruple the quantity of active sites of Ni/MgAl₂O₄, and the promoting effect increased with a higher Ir loading. The bimetallic Ir₁₀Ni₉₀/MgAl₂O₄ catalyst achieved CH₄ and CO₂ conversion of 95% and 98%, respectively, at 1 bar; and was able to maintain a relatively high CH₄ and CO₂ conversion of $\sim 60\%$ when pressurized to 20 bar.

2.2.2 Ni-based catalysts promoted by non-noble metals

Despite multiple advantages, the use of noble metals is still constrained for economic reasons. Therefore, many researchers have turned to the application of non-noble metals as potential promoters of Ni-based catalysts.

Ni-Fe-based catalysts/oxygen carriers have been tested for chemical looping steam methane reforming (CL-SMR). Hu et al. [63] used Ni-Fe modified calcite as an oxygen carrier and concluded that a Fe/Ni ratio of 0.67 was optimal for the reaction, while higher Fe concentration led to sintering. The novel material exhibited good catalytic performance with the highest CH₄ conversion of 98.9%, and high stability during the long-term reaction process. Garai et al. [64] tested Ni-ferrite supported on ZrO₂ and CeO₂, which showed high H₂ and CO selectivity, as well as high CH₄ conversion (93%, 98%, and 99%, respectively). No carbon deposition was observed on the used material, due to the ability of iron oxides (FeO_x) to remove carbon via a surface redox cycle to produce Fe and CO₂ [65]. Djaidja et al. [66] reported that although the addition of Fe slightly decreased the CH₄ conversion of the (Ni-Mg)₂Al catalyst from 93% to 91%, both H₂ and CO yield were improved and carbon formation was significantly suppressed.

In addition, the Fe-promoted Ni catalyst was also proved to be sulphur-resistant. Tsodikov's team [67, 68] tested Ni-Fe/ γ -Al₂O₃ catalysts prepared by epitaxial coating and a novel core-shell type catalyst containing Ni and Fe (Figure 2-2) under SMR conditions in the presence of up to 30 ppm H₂S. The materials showed good catalytic activity, unlike conventional Ni-based catalysts, which lose activity rapidly when the gas-vapour mixture contains H₂S. This property was attributed to the core-shell structure, in which the core containing Ni-Fe

nanoparticles provided the catalytic ability while the $\gamma\text{-Fe}_2\text{O}_3$ shell provided vacancies for H_2S to decompose to elemental sulphur following the reactions below:

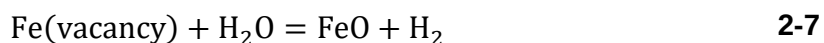
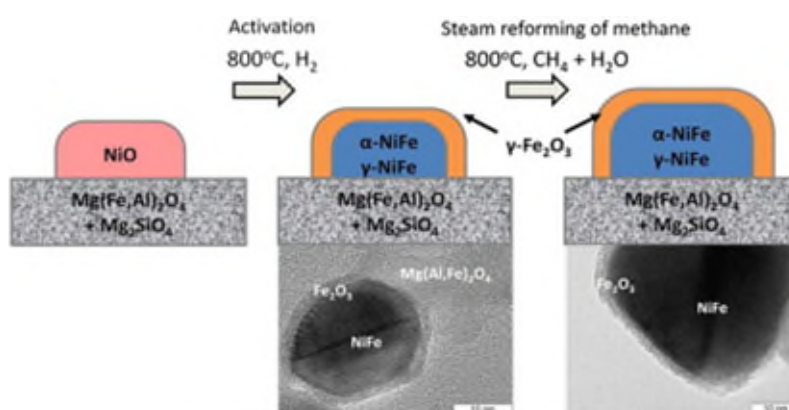


Figure 2-2 Core-shell configuration with the Ni-Fe alloy core surrounded by a superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$ shell. Reprinted from [67] with permission from Elsevier.

Cobalt is also considered a promising SMR catalyst additive because of its good activity for the WGS reaction, which assists in shifting the equilibrium towards higher H_2 production. However, one problem related to the usage of Co is its tendency to oxidize when the temperature and steam partial pressure are in the range used for SMR [69]. Alloying it with Ni is a potential solution to this problem while preserving the advantages of both elements. A series of Ni-Co/ ZrO_2 bimetallic catalysts with different Co loadings were tested and compared to monometallic Ni and Co catalysts by Harshini et al. [70]. Their results suggested that a Ni/Co ratio of 1:1 was optimal for limiting both oxidation of Co and carbon formation caused by Ni. The material also exhibited long-term stability with a constant CH_4 conversion of 81.8% within 50 h with no surface carbon formation. You et al. [71] tested a series of Ni-Co/ $\gamma\text{-Al}_2\text{O}_3$ catalysts and found that at a temperature of 800 °C Co-modified catalysts exhibited the same reforming activity as unmodified ones with enhanced coke resistance. The performance of the bimetallic catalyst was not as good as Ni at low temperatures, possibly due to the formation of Ni-Co alloy, which increased the crystallite and particle size of the material, while decreasing metal dispersion and surface area, and

blocking low-coordinate active Ni sites where the rate-determining CH₄ dissociation step takes place.

Ni-Cu bimetallic catalysts have been used for the conventional SMR process [60] as well as low-temperature SMR [73–75]. Results showed that by adding Cu as the promoter, a larger Ni crystallite size, surface area, and better metal dispersion were obtained [74], and the overall carbon resistance of the material was enhanced [66,72]. TGA results before and after a long-term SMR test (20 hours) showed that carbon formation on Ni-Cu/Al₂O₃ was greatly suppressed (8.9%) compared to commercial Ni/Al₂O₃ (28.3%). The addition of Cu has also been proven to enhance the activity of the WGS reaction [76], which explains the increase in CH₄ conversion when using Cu-Ni as the catalyst. However, it should be noted that an upper limit exists in terms of the promoting effect of Cu. A Cu/Ni ratio equal to or higher than 5 in the material will result in reduced catalytic activity, as reported by Huang et al. [73].

The promoting effect of Zirconium was investigated by Lertwittayanon et al. [77] using Ni/ α -Al₂O₃ catalysts containing CaZrO₃ nanoparticles. CaZrO₃ loading between 10 and 15 wt.% showed the best catalytic performance with a CH₄ conversion of 67%. Results also showed that unlike conventional SMR catalysts requiring an S/C ratio of approximately 3, an S/C ratio of 1/3 or 1 was most appropriate for the CaZrO₃-modified catalyst. This is because a high S/C ratio causes an excessive amount of steam to adsorb on the CaZrO₃ surface, which competes with the adsorption of CH₄.

Boudjeloud et al. [78] tested a series of La-promoted Ni/ α -Al₂O₃ catalysts. The highest CH₄ conversion (97%) and H₂ yield (94%) were obtained with a Ni/La ratio of 7:3. The improved activity compared to monometallic Ni was credited to the decrease in Ni particle size and enhanced metal dispersion, which prevented the agglomeration and sintering of the bimetallic material. The addition of La also facilitated the reduction of Ni, however, its effect on coke resistance was not significant [27].

The effect of doping Molybdenum was studied by Maluf and Assaf [79] using Mo-Ni/Al₂O₃ catalysts with different Mo concentrations. The addition of Mo decreased the surface area of the catalyst, possibly due to the blockage of active Ni sites by MoO_x. However, the specific activity of each active site was increased, which was attributed to the transfer of electrons from MoO_x to Ni particles resulting in an increase in electron density in Ni. Molybdenum carbide has also been employed in the methane reforming process and is known to have good catalytic activity and stability at high pressures [80]. However, its stability quickly drops

at atmospheric pressure due to the surface oxidation of Mo_2C to MoO_x by CO_2 . This problem can be mitigated by combining Mo_2C with nickel. Despite being a major reason for the deactivation of traditional Ni catalysts, carbon deposited on the bimetallic Ni- Mo_2C surface promotes the carburization of NiMoO_x back to its carbide form [81,82]. Ni- Mo_2C catalysts have been tested for dry methane reforming [81–83], steam reforming of methanol [84], as well as steam- CO_2 bi-reforming of methane [85], and have shown more promising results than unpromoted Mo_2C catalyst or Ni-Mo catalyst in their reduced form.

The promoting effect of the rare earth element, rhenium, was reported by Xu et al. [86]. They concluded that by coating a Ni-Re bimetallic layer on the surface of a high cell density Ni monolith catalyst, the reducibility and catalytic performance of the material were enhanced. The low hydrogen adsorption energy of Re atoms also facilitates the adsorption of hydrogen atoms on Re and adjacent Ni atoms, which suppresses the oxidation of Ni and leads to enhanced catalyst stability.

2.2.3 Ni-based catalysts promoted by metalloids

Silicon is one of the most studied metalloids as it is often employed as the catalyst support for the SMR process, usually in its oxide or carbide form, because of its thermal stability and potentially high surface area. Silica is generally considered an inert material, as it has weak metal-support interaction with the active metal (Ni in most cases) due to its low reducibility [87]. The lack of metal-support interaction in Ni/ SiO_2 is also a source of filamentous whisker carbon formation [88]. To improve the interaction between Ni and the silica support matrix, Majewski et al. [89] synthesized a core-shell typed Ni/ SiO_2 catalyst using the Stöber-deposition-precipitation method and tested it under different SMR conditions. Results showed that the core-shell structure increased the coke resistance of the catalyst, as deposited carbon was only detected at a low s/c ratio (1:1) and temperature (550 °C). Other characteristics of the support material, including crystallite size and metal dispersion, are affected by the acidity/basicity of the support and are also known to influence the rate of carbon growth on the catalyst surface. The acidity of the silica support facilitates the decomposition of methane, but at the same time promotes cracking and polymerization leading to catalyst deactivation because of carbon formation [88]. To achieve a better acid-basic balance, basic metal oxides, including ceria [90,91] and magnesia [92,93] are often added to Ni/ SiO_2 to tune the surface acidity of the support, and it was found that a homogeneous distribution of the basic sites on the acidic silica framework improved the long-term stability of the catalyst.

Elements with a similar electronic structure of carbon include tetra- and penta-valent *p* such as Sn, Sb, As, Ge, Pb, Ag, etc. The addition of these metals was predicted to have a coke-resisting effect, because, similar to the formation of nickel carbide (interaction between $2p$ electrons of carbon and $3d$ electrons of Ni), the reaction between these metals with Ni could potentially reduce the chance of Ni-C interaction. A few of the above candidates were tested by D.L. Trimm [94], and their coke-resistant ability followed the order of As > Ag > Sb > Sn > Pb.

The addition of Sn was also investigated by Nikolla et al. [95–97] experimentally and numerically. The bimetallic Ni-Sn catalysts showed lower CH₄ conversion during the first 30 minutes of the reaction, however, its long-term stability was greatly enhanced. The carbon resistance of the Ni-Sn/YSZ catalyst was explained by DFT calculated reaction energy barriers, which showed that the Ni-Sn alloy surface preferentially oxidizes C* rather than forming C-C bonds. The presence of Sn also lowers the binding of C* to low-coordinated sites, which is the position for carbon nucleation. The decrease in the catalytic activity of Ni-Sn alloy is possibly due to the blockage of low-coordinate Ni sites by Sn, as these sites are the most active for the rate-determining C-H bond activation step.

Similar to Sn, boron-promoted Ni catalyst has also demonstrated good stability due to the reduction in carbon nucleation centres. A boron loading of 1 wt.% was sufficient to enhance the overall stability of the material without compromising its catalytic activity [98]. Apart from this, Ligthart et al. [27] also reported the structural-promoting ability of boron to obtain small Ni particles. However, one limitation of the bimetallic material is that the addition of boron strongly impeded the reduction of Ni.

Apart from the experimental work mentioned above, the SMR activity of metalloid-promoted nickel catalysts was also studied using numerical methods. In the work by Xu et al. [21], the catalytic activity of a series of bimetallic alloys was predicted based on a microkinetic model, and DFT-calculated atomic adsorption energies on the bimetallic M₁M₂(211) surface. By setting the conditions as 793 °C, 12.2 bar, and with gas composition as 50% to equilibrium, alloys including Ni₃M (M = Sn, Sb, Ge, and As) and Co₃Ge were predicted to have the highest activity (Figure 2-3). Although these elements showed promising results, experimental validation of the *in-silico* study has not been found. Further study can be carried out on these metalloids (Sb-, As-, and Ge-based catalysts) in search of an optimal balance between activity and stability.

Although Co is less prone to coke formation compared to Ni, the interaction between Co and the metal oxide support is strong, leading to the formation of cobalt oxides with limited reducibility [101]. As presented in section 2.2.1, by adding a small amount of noble metal the reducibility of the transition metal-based catalysts can be largely improved because of the hydrogen spillover effect. Profeti et al. [102] explored the effect of noble-metal promoters (0.3 wt.% Pt, Pd, Ru, and Ir) on Co/Al₂O₃ catalysts. Results showed that the addition of the noble metals significantly decreased the reduction temperature of cobalt species, with their promoting effect following the order of Pd > Pt > Ru > Ir. In terms of their catalytic activity, the Co-based bimetallic catalysts did not show satisfying results. Average CH₄ conversion of 50-60% was obtained for Pd-, Pt- and Ir-Co, 30% for Ru-Co, and only 7% for Co/Al₂O₃, which was possibly due to the partial oxidation of cobalt active sites in the presence of water molecules.

Akbari-Emadabadi et al. tested a Ca-Co bifunctional catalyst/sorbent (with a mass ratio of Ca/Co = 9) in the CL-SMR process, and investigated the promoting effect of yttrium [103] and zirconium [104], with a mass ratio of Ca/Y = Ca/Zr = 4.5. Both promoted samples remained stable at 700 °C for up to 16 redox cycles, whereas the unpromoted one was deactivated after 10 cycles. The catalytic performance of the materials is summarised in the table below (Table 2-2). Both Y and Zr showed a promoting effect regarding catalytic activity for SMR and H₂ selectivity, and the usage of Zr was more advantageous in comparison to Y. Based on the results from catalyst characterization, the addition of Co reduced the overall surface area of the material by more than 30%, whereas the addition of Zr compensated this negative effect to some extent. Results also showed that Zr prevented the formation of Ca₂Co₂O₅ spinel in the structure of the bimetallic material, which lowered the risk of losing active sites of Co. The study proved Y and Zr to be promising textural promoters of the bifunctional catalyst/sorbent materials employed in CL-SMR.

Table 2-2 Comparison between the catalytic activity of unpromoted and promoted Ca-Co samples.

	CH ₄ conversion (%)	H ₂ yield (%)	H ₂ /CO ratio
Unpromoted Ca-Co	95.0	81.5	5.2
Ca-Co-Y	95.8	82.9	5.3
Ca-Co-Zr	98.3	84.7	10.0

Apart from Co-based bimetallic catalysts, catalysts combining two types of noble metal have also been studied. The research by Roy et al. [105] focused on a novel Pt-Rh (1.2 wt.%) catalyst supported on metal foam. The sample was tested in a multichannel heat exchanger platform reactor to evaluate its potential in solid oxide fuel cell application. The combination of Pt and Rh was proven to enhance the production of hydrogen by SMR, with CH₄ conversion, H₂ yield, and H₂/CO ratio of 97.2%, 3.16 mol per mol of CH₄ input and 6.03, respectively, all of which were higher than commercial monometallic Ni and Ru catalysts. The novel catalyst also showed excellent stability, negligible coke deposition was found after 200 h of SMR reaction at 800 °C. Further research from an economic point of view should be carried out to evaluate the potential of these materials in large-scale applications.

2.4 Polymetallic catalysts

Compared to the relatively simple mono and bimetallic systems, the application of catalysts containing three or more types of active metals in SMR has not been investigated in detail. Existing literature mainly examined Ni-based material with the addition of two or three commonly used elements, such as Co, Cu, Ru, Pt, etc.

The effect of the simultaneous presence of copper and zinc in Ni/Al₂O₃ catalyst was investigated by Nazari and Alavi [106]. They reported that Cu and Zn affect the Ni-based catalyst in different ways – Cu enables a better resistance to coke formation while Zn improves the catalyst's activity, stability, and H₂ selectivity. The optimal combination of the three metals for SMR was found to be 15%Ni–1%Cu–5%Zn, which achieved a CH₄ conversion of 94% and an H₂ yield of 3.12.

Jeon et al. [107] investigated the performance of a selection of bi- and trimetallic Ni-based catalysts under steam-deficient conditions. A series of bimetallic catalysts containing 5 wt.% of alkaline earth metal (Mg, Ca, Sr, Ba) or 0.5 wt.% noble metal (Ru, Rh, Pt, Pd), and trimetallic catalysts containing both alkaline earth metal and Ru were synthesized. Results from the tests demonstrated that adding Mg or Ca enhanced the coke resistance of Ni-based catalysts, whereas the effect of Sr and Ba was not significant. Among the noble metals, Ru was the best candidate for suppressing coke deposition. Based on these conclusions, a catalyst with optimized composition – 0.5%Ru-5%Mg-10%Ni/γ-Al₂O₃ – was selected and tested. A CH₄ conversion of 96% was maintained for 250 h, proving its excellent long-term stability.

Bi-functional polymetallic materials combining the catalytic ability of transition metals and CO₂ sorbents are commonly employed for the SESMR process [108]. Chen et al. [109][110]

found that a simple physical mixture of Ni/Al₂O₃ (20 wt.%) and CaO was able to improve H₂ purity to above 95%, compared to 72% without in-situ CO₂ removal. Based on an elemental mapping analysis of the samples, each Ni elemental point was surrounded by several Ca points, which allowed the efficient capture of CO₂ produced during the reaction.

Dewoolkar and Vaidya [111] synthesized hybrid Ni-CaO/Al₂O₃ and Ni-hydrotalcite materials by coprecipitation and incipient wet impregnation, respectively. The materials were tested at T = 500 °C with an S/C ratio of 9 for 20 cycles for stability evaluation. Results showed that CH₄ conversion and H₂ yield of the hybrid materials were higher than those obtained using a physical mixture of catalyst and sorbent, due to the more efficient mass and heat transfer. The hybrid materials also exhibited better stability, Ni-CaO/Al₂O₃ and Ni-hydrotalcite maintained high H₂ purity of 90% for up to 11 and 16 cycles, respectively, compared to the sintering and deactivation of the mixed material after only 2 cycles.

Di Giuliano et al. [112,113] reported the use of mayenite as for bi-functional Ni-CaO material. Results from multicycle sorption/regeneration TGA demonstrated the stable sorption capacity of the material after 20 cycles. This enhanced stability compared to commercial CaO was attributed to the presence of mayenite as an inert binding, preventing CaO from sintering. The same phenomenon was also observed by Dang et al. [9], confirming the role of mayenite as a structural stabilizer. Di Giuliano et al. also concluded that the nickel precursor used for material synthesis may affect the texture and reducibility properties, and nickel nitrate hexahydrate was found to be the most suitable precursor.

Kim et al. used ruthenium as the reforming catalyst and tested the performance of Ru-CaO/Ca₃Al₂O₆ under SESMR conditions [114]. As Ru is a highly active catalyst for SESMR, the mass fraction of CaO was able to be increased significantly compared to conventional Ni-CaO-based materials. Ca₃Al₂O₆ acted as the structural stabilizer against sintering, and maintained the surface area of Ru-CaO/Ca₃Al₂O₆ at 18 m²/g after 10 cycles of SESMR, compared to 5 and 6 m²/g for Ru/lime and Ru/CaO.

Hafizi et al [115] modified conventional calcium-based CO₂ sorbent with CeO₂ and tested it for CL-SESMR together with Co₃O₄/SiO₂. The addition of CeO₂ significantly improved the morphology of CaO by increasing its surface area and uniformly distributed pores in the sorbent structure. Combined with the Co-based catalyst, the material was able to produce high-purity H₂ (93 – 96%) for 8 redox cycles and maintain the same CO₂ removal efficiency for 3 carbonation/calcination cycles.

Ghungrud et al. [116] reported a novel trimetallic bi-functional material for SESMR, consisting of Ni and Co (with concentrations varying from 0 to 40%) supported on hydrotalcite and promoted by 2.5 wt.% cerium. The hybrid material was evaluated in terms of its H₂ production ability, sorption capacity, and cyclic stability. Results revealed that CH₄ conversion increases with the Co content in the material, which is possibly due to the enhancement of WGS reaction by Co. Under optimal reaction conditions, CH₄ conversion of 95.7% and 90.7% were obtained by two Ce-promoted Ni-Co samples (with Ni/Co ratios of 1/3 and 1, respectively). The maximum sorption capacity was found to be 1.74 and 1.51 mol CO₂/kg, respectively. The material was also tested at optimal conditions for 25 cycles, samples showed good stability by maintaining an H₂ concentration higher than 90% and remained stable for 21 and 16 cycles. This property was attributed to the effective metal-support interaction and higher active metal dispersion within the promoted material. The author concluded that the hydrotalcite-supported Ce-Ni-Co (2.5, 10, 30 wt.%) trimetallic catalyst/sorbent shows good performance and could be a promising candidate for large-scale SESMR application.

Similarly, Dewoolkar and Vaidya investigated the promoting effect of Ce and Zr on a Ni/hydrotalcite bi-functional material [117]. Results showed that both Ce and Zr were able to increase the surface area and surface basicity, which inhibited coke formation. Both Ce and Zr-promoted materials remained stable for 13 and 17 cycles, respectively, whereas the unpromoted material became unstable after 9 cycles. The addition of Ce was particularly beneficial, as the promoted bi-functional material reached a high CH₄ conversion of 96.4% and an adsorption capacity of 1.41 mol CO₂/kg sorbent.

Apart from the type of promoter added to Ni-based catalysts, the structure of the promoted catalyst also influences its overall performance. Cho et al. [118] synthesized a bimetallic catalyst with a novel egg-shell structure by selectively placing Ni and Ru on the shell of alumina. Three types of catalysts were compared, including (a) egg-shell-type bimetallic catalyst (5 wt.% Ni + 0.7 wt.% Ru / Al₂O₃), (b) monometallic 1 wt.% Ru/Al₂O₃ catalyst with the same egg-shell structure, and (c) monometallic 1 wt.% Ru/Al₂O₃ synthesized by the conventional wet impregnation method. The comparison between (b) and (c) showed that the novel structure was able to improve methane conversion and maintain it at a higher level when gas hourly space velocity was largely increased. This was because the novel structure enables the active metal, ruthenium, to be mainly deposited on the outer region of the alumina pellets and can therefore be utilized more efficiently. With the addition of nickel, (a) achieved an even higher methane conversion than (b) at higher gas hourly space velocity.

This proved that the novel structure enables the efficient utilization of active noble metals, reducing the metal loading necessary and, therefore, the overall cost.

Obradovic et al. [119,120] proposed a novel plate-type catalyst for SESMR, as demonstrated in Figure 2-4. This material was synthesized by depositing Pt and Al₂O₃ on a static mixer element made of Ni alloy. During the SESMR process, it acts simultaneously as the catalyst, the distributor for solid sorbent, as well as the gas-phase radial mixer. The CH₄ conversion obtained by this novel catalyst was 15 times higher than monometallic Ni under the same conditions. However, its catalytic activity rapidly decreased after 10 h of reaction, temperatures higher than 590 °C also led to activity loss due to carbon accumulation on the material surface. Further investigation on modifying relevant parameters (such as the promoter type, metal loading, and reaction conditions) to increase its stability may be of interest.

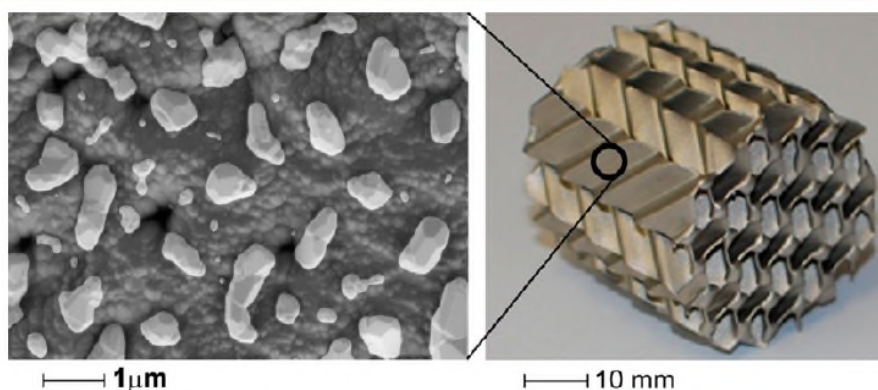


Figure 2-4 Plate-type Pt-Ni/Al₂O₃ catalyst. Reprinted from [119] with permission from ACS.

Based on the above review, it can be concluded that an increase in catalytic activity is usually achieved either by modifying the textural properties of the material (e.g. increasing surface area and metal dispersion) using a second active metal; or by modifying the energetics of the surface reactions, in particular the rate-determining step (e.g. decreasing activation energy of the first C-H bond in CH₄ dissociation). Although a variety of metal combinations have been studied for their performance in the SMR reaction, there exist many other combinations of elements that have been predicted to be active or have not been evaluated at all regarding their reforming activity.

2.5 Catalyst synthesis

The synthesis of bimetallic catalysts involves various methods, each offering unique advantages and challenges. These synthesis routes can be broadly divided into two categories – physical methods (e.g. co-precipitation, impregnation) and chemical methods

(e.g. galvanic replacement, chemical vapor deposition). Different synthesis methods and conditions usually result in different compositions, structures, and morphology of the catalysts, influencing their catalytic performance. Understanding and harnessing these synthesis strategies are crucial for tailoring bimetallic catalysts for the SMR process. In this section, a summary of commonly used synthesis methods for bimetallic SMR catalysts is provided, and the advantages and limitations of each method are analysed before a synthesis method is selected for the catalysts involved in this work.

2.5.1 Co-precipitation

Co-precipitation is one of the most commonly used methods for the synthesis of bulk bimetallic catalysts. The process involves the simultaneous precipitation of two or more metal ions from a solution, resulting in the formation of a mixed metal oxide or hydroxide, which upon further treatment (e.g. calcination, hydrogen activation), yield the desired bimetallic catalysts. A schematic diagram of the co-precipitation method is presented in Figure 2-5, where Na_2CO_3 is used as the precipitation agent. The co-precipitation method offers several advantages, including its simplicity, low-temperature requirement, and easy control of particle size and composition [121]. Nonetheless, it also presents some challenges, including the precipitation of trace impurities and batch-to-batch reproducibility issues.

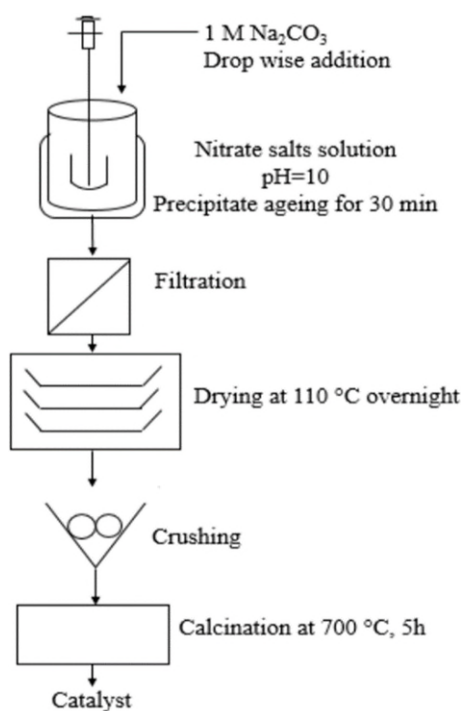


Figure 2-5 Schematic diagram of the co-precipitation method [122].

Jimenez-Gonzalez et al. [123] prepared a series of $\text{NiAl}_2\text{O}_4/\text{Al}_2\text{O}_3$ catalysts using the co-precipitation method. Compared with the samples synthesized using alternative methods, these catalysts exhibited smaller particle sizes, higher metal dispersion, and metallic surface, which were beneficial for achieving a high SMR activity. Similar observations were made by Qi et al. [124], where the co-precipitated Ni/Mg-Al catalyst achieved much higher activity as a result of higher specific surface area and better Ni dispersion.

2.5.2 Co-impregnation

An equally common and popular technique for bimetallic catalyst synthesis is the impregnation method. In this process, two or more metal precursors are thoroughly mixed before being deposited onto a support material (e.g. alumina), allowing for the simultaneous incorporation of multiple metals into the catalyst structure. The main advantages of the co-impregnation method include its simplicity, precise control over the stoichiometry and composition of the bimetallic catalysts, and the uniform distribution of multiple metal elements on the support material. However, one major drawback of this method is the lack of size control [125].

The co-impregnation method has been used in various studies for the synthesis of bimetallic catalysts, including Ni-Co-based [126], Ni-Ca-Zr-based [127], Ni-Pt-based [128,129], and Ni-Ce-based [128,129]. In all cases, even distribution of the active metals within the catalyst support structure was observed. It was also found that the co-impregnation method promotes the metal-support interaction to prevent the oxidation of the active Ni^0 species in the catalyst, and at the same time, allows for the high dispersion rate of Ni^0 on the support surface to increase its overall activity [130].

2.5.3 Sol-gel method

Another widely employed method for bimetallic catalyst synthesis is the sol-gel method. In this process, a “sol”, which is a solution containing metal precursors, undergoes hydrolysis or condensation, to form a gel containing interconnected nanoparticles. By altering the gel formation temperature, different types of gels can be formed (e.g. aerogel, xerogel, and cryogel), each with distinctive properties. A schematic diagram of the sol-gel process is presented in Figure 2-6. The main advantages of the sol-gel methods include the high purity of the product, the narrow size distribution of the pores within the product, and a uniform nanostructure [131]. However, a major drawback is the shrinkage of the wet gel upon drying, which may lead to fracture.

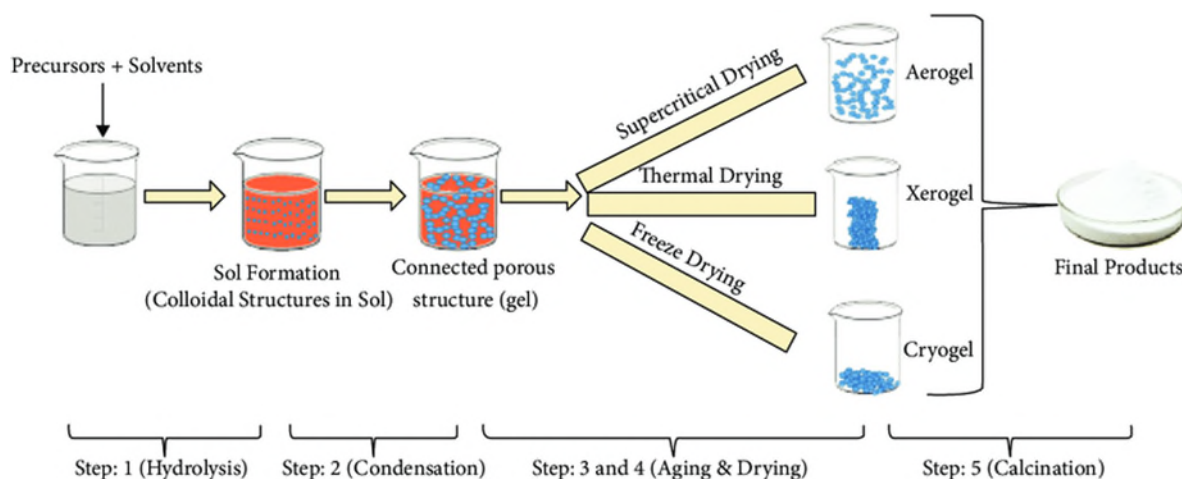


Figure 2-6 Schematic diagram of the sol-gel method [131].

Li et al. [132] tested a Cu/ZnO/Al₂O₃ catalyst synthesized by the sol-gel method for Methanol steam reforming. The material showed superior mechanical strength compared to the commercial catalyst with the same composition. Polymetallic catalysts synthesized by the sol-gel method were tested for SMR by Itkulova et al. [133]. The sol-gel process allowed for the high dispersion of the metal oxides and microalloys within the support structure, which contributed to their high activity and stability. The difference between the sol-gel method and the conventional impregnation was investigated by Aghamohammadi et al. [134]. They concluded that smaller particle size, more even size distribution of the particles, and better metal dispersion could be achieved by employing the sol-gel method.

2.5.4 Other methods

Apart from the previously mentioned methods, other more advanced techniques have also been employed for the synthesis of bimetallic catalysts. A summary of each technique is provided below:

- **Electrodeposition:** This process involves the sequential electrodeposition of metal cations in a metal salt solution, while a voltage is applied. This method is usually used for synthesizing catalytic electrolytes involved in electrochemical processes [135], including fuel cells and electrochemical sensors, or for the synthesis of single-atom catalysts [136]. Electrodeposition is a green and fast method, capable of achieving good metal dispersion and chemical stability. However, due to the necessity of electric voltage, the cost and requirements of the method are relatively high [137].
- **Chemical vapour deposition:** This process involves introducing metal precursors and reactant gases into a chamber where chemical reactions take place to coat the desired metals onto a substrate surface. This method is usually used when the

deposition of metals on the support or a structured catalytic reactor needs to be precisely controlled [138]. Due to the specialised equipment required for this process, chemical vapour deposition is sometimes limited by its cost and complexity [139].

- **Atomic layer deposition:** Similar to chemical vapour deposition, this method offers precise control over the thin metal layer deposited on the substrate surface at the atomic scale. It allows for delicate structural design and precise material composition to be achieved, contributing to the enhanced activity, selectivity, and stability of the catalyst [140]. However, this method is seldom used for the production of bulk catalysts due to its complexity and high requirement of reaction conditions.

The catalysts studied in this work include bimetallic Ni-Cu, Ni-Fe, and Ni-Ge supported on Al_2O_3 support. considering the pros and cons of each synthesis method, wet-impregnation was selected as it is suitable for pelletized support materials and offers a uniform and high dispersion of the active metals.

2.6 Sorbents for SESMR

As previously mentioned in section 2.1, in the SESMR process, a sorbent material is introduced into the reformer reactor, which selectively removes carbon dioxide from the reforming gas mixture, thereby shifting the equilibrium of the reforming reaction towards increased hydrogen yield. This simultaneous removal of carbon dioxide leads to higher-purity hydrogen production and reduces the energy required for downstream separation processes. In this section, commonly used sorbent materials for the SESMR process are summarized and critically reviewed. Recent developments in SESMR are also highlighted, showcasing pilot-scale demonstration projects conducted both in the UK and globally.

2.6.1 Sorbent materials

2.6.1.1 Calcium-based sorbents

Ca-based sorbents play a vital role in SESMR, as they are by far the most commonly used sorbent material. Calcium oxide is an excellent CO_2 sorbent with a high sorption capacity (78.6 g_{CO_2} per 100 g_{CaO} [141]). Its availability and low cost also make it the ideal option for large-scale in-situ carbon capture processes. CaO-calcium aluminate-based sorbents have been extensively studied for SESMR, using conventional Ni-based materials as catalysts [142]. In the presence of these sorbents, methane conversion can usually reach over 95%, and the optimal reaction temperature was found to be around 650 °C [143,144]. The sorbents were tested for more than 10 consecutive SESMR/regeneration cycles, and the

methane conversion was found to be higher than 90% with only a moderate decrease in CO₂ sorption capacity [145,146].

2.6.1.2 Magnesium-based sorbents

Magnesium oxide is also frequently utilized in SESMR processes. Similar to calcium oxide, magnesium oxide absorbs CO₂ through chemical reactions and releases it when heated. MgO-based sorbents have been tested for their sorption performance and were concluded to be effective for low-temperature CO₂ capture [147,148]. MgO is also widely used as an additive to calcium-based sorbents to form dolomite. Multiple studies have investigated the performance of CaO/MgO sorbents in sorption-enhanced hydrogen production processes [149–151]. The cyclic stability of the CaO-based sorbent was found to be significantly enhanced, which was attributed to the inhibited sintering of CaO by the addition of MgO. The addition of MgO was also found to increase the dispersion of CaO through the formation of MgCa(CO₃)₂ precursor, thus inhibiting the agglomeration of large CaO particles which leads to sintering [152].

2.6.1.3 Hydrotalcites

Hydrotalcite, also known as layered double hydroxide, is a class of synthetic or naturally occurring compounds with a layered structure. Hydrotalcite materials are considered to be suitable sorbents due to their good CO₂ sorption capacity (0.45–1.0 mol CO₂/kg [153]). The ideal temperature range for CO₂ sorption using hydrotalcite is generally considered to be between 400 – 500 °C [153,154]. However, this may pose problems to its application for the SESMR process, as the SMR reaction is endothermic, and a more elevated reaction temperature (600 – 800 °C) is generally needed. A series of hydrotalcite materials with different compositions have been tested for SESMR, including but not limited to NiMgAl-based hydrotalcite [155], waste-derived CaO-promoted MgNiAl hydrotalcite [156], and MgAl-based hydrotalcite [157]. It was found that hydrotalcite sorbents are able to improve the purity of the hydrogen produced to up to 80 – 99%. However, the difference in the [153]sorption capacity of each type of sorbent is significant due to the large span of hydrotalcite composition and preparation method [153].

2.6.1.4 Combined Sorbent Catalyst Materials

Combined Sorbent Catalyst Materials (CSCM) have gained increasing attention as a dual-functional material for the SESMR process. These materials are designed to simultaneously capture CO₂ and catalyse the SMR reaction. CSCMs offer several advantages over conventional sorbent materials, including lowered mass transfer resistance, reduction in

reactor volume, and a more simplified reaction system [158,159]. Mayenite-based CSCMs are by far the most commonly tested materials [160–164]. They were shown to exhibit high stability for over 200 SESMR/regeneration cycles. The high CO₂ sorption capacity was attributed to the effective sorption of CO₂ by mayenite, while at the same time, the finely dispersed active metal (e.g. Ni) on the CSCM structure did not negatively affect the performance of the sorbent. The highly dispersed nickel also reacts with the mayenite to form NiAl₂O₄ spinel, which can be easily reduced under relatively low temperatures (400 – 600 °C) to produce the active Ni particles.

2.6.2 Recent developments in SESMR

As an emerging novel technology, SESMR is currently at Technology Readiness Level (TRL) 4 [8]. Several projects are currently underway to take the TRL of the SESMR technology to the next level. A 1.5 MW pilot plant is currently under construction at Cranfield University (UK), which aims to demonstrate the process as an integrated system for future commercial deployments [165]. The system operates at 24 bar, using a bubbling fluidised bed as the reformer/carbonator and an entrained flow reactor as the calciner. It is estimated that the system will be able to achieve a CO₂ capture rate of ~97% and an over 50% reduction in CAPEX with similar OPEX. A similar plant with a smaller scale (71 kW) has been constructed in the USA by GTI [166]. A hydrogen purity of over 80% was achieved, with a 12 – 40% decrease in CAPEX and a 20% decrease in OPEX compared to the conventional SMR process. Another pilot plant with a similar scale (30 kW) was built by the IFE Hynor Hydrogen Technology Center in Norway [167]. The system consists of a dual bubbling fluidized bed reactor that produces hydrogen through SESMR, integrated with a high-temperature solid fuel cell system. A high purity (~95%) hydrogen stream was obtained with a high carbon capture rate.

Although both bench-scale and pilot-scale demonstrations have shown SESMR as a promising technology for the production of high-purity and low-carbon hydrogen, further studies are needed to optimize process efficiency, enhance scalability, and address potential challenges related to the future commercialization of the technology.

2.7 Conclusions and outlook

SMR is currently the most dominant hydrogen production technology, and extensive research on the catalytic aspect of this process has been carried out. Carbon emissions from SMR can be reduced by adding a CO₂-sorption step. This review provides insights on recent developments in the use of bi/polymetallic catalysts for (SE)SMR. The performance

of the bi/polymetallic catalysts presented in this review is briefly summarized in Table 2-3 and is evaluated based on three main factors: stability (resistance to carbon, sulphur, sintering, and oxidation), catalytic activity and selectivity, as well as their physical/chemical properties (reducibility and self-activation ability).

The most widely used SMR catalyst to date is ceramic-supported nickel because of its relatively good performance and inexpensive price, but problems such as sintering and coke formation still exist. In search of catalysts with better performance, various elements have been added as promoters to conventional Ni-based catalysts. Noble metal-promoted catalysts generally have superior reactivity, coke resistance, and enhanced reducibility, but their applications are often limited by their prices. Researchers have therefore turned to non-noble metals and metalloids. The addition of iron was found to be coke and sulphur-resistant due to the surface redox reaction between Fe^0 and FeO_x . Both cobalt and copper can enhance the activity of the WGS reaction, thus shifting the reaction towards more hydrogen production. Elements including zirconium, yttrium, and lanthanum were found to be good textural promoters due to their ability to increase the surface area and metal dispersion of the material. Silicon is often used as the catalyst support in its oxide or carbide form, and the addition of ceria or magnesia was able to tune the surface acidity of silica for better long-term stability. The addition of other metalloids (tin, boron) led to enhanced coke-resisting ability, but often at the expense of losing catalytic activity. A DFT-based study has also predicted germanium, arsenic, and antimony to be effective promoters of nickel-based catalysts, however, further experimental verification is still necessary.

Apart from the type of element selected as the promoter, the loading of each component is also a critical parameter that influences the overall performance of alloy material. A higher active metal loading does not necessarily indicate a higher activity due to the restricted distribution of active metal in the material. The influence of material structure on catalytic activity was also investigated. Although novel core-shell type, plate type, and metal foam-support structures were found to be beneficial to the overall catalytic performance, this largely complicates the synthesis process and limits the wide application of the materials. It is, therefore, necessary to find a balance between improvements to the material properties and a viable and efficient material preparation process.

The SESMR technology has been identified as a promising alternative to the conventional SMR process. With the addition of a solid sorbent (usually Ca- or Mg-based) or by integrating the sorbent with the catalyst to form a CSCM, the purity of the hydrogen produced can be significantly increased. However, scale-up experiments are needed to assess the feasibility

of the SESMR technology for industrial-scale applications, considering factors such as reactor and material design and production economics.

Table 2-3 A summary of bi/polymetallic catalysts for SMR. (Green/Red: promoter has a positive/negative effect on the overall performance, compared to the monometallic base material. Blank: no data available. *: result based on numerical modelling.)

Base material	Promoter(s)	Catalyst stability			Catalyst performance			Physical/chemical properties	
		Carbon resistance	Sulphur resistance	Sintering resistance	Resistance to metal oxidation	Catalytic activity	H ₂ selectivity	Self-activation	Reducibility
Ni	B	[98]				No significant effect [98]			[27]
	Fe	[63][66]	[67,68]			Slight decrease [66]	[64][66]		
	Co	[70,71]			[69]	[71]			
	Cu	[66,72]				[73]	[73]		[75]
	Ge					*[21]			
	As	[94]				*[21]			
	Zr					For low S/C (1/3) [77]			[77]
	Mo				[80]	[79]			
	Ru	[22,23]			[39,40]	[24,25]		[24,25]	[22]
	Rh	*[23]		[28]	[41,42]	[26,27]	[29]	[41,42]	[26,27]
	Pd	[26–31]				[33–38,168]		[42]	[33–38,168]
	Ag	[45,48,49,169, 170]				[170]			
	Sn	[95–97]				[97]			
	Sb	[94]				*[21]			
	Re				[86]	[86]			[86]
	Ir	[62]		[28,62]		[28,62]			
	Pt				[42–44]	[171,172]		[42–44]	[42–44]
	Au	*[52,53,173]; [54,55]	[61]			*[52,53,173]; [54,55]			[61]
	La	No significant effect [27]		[78]		[78]			[27]
	Cu + Zn	[174]				[174]	[174]		
	Co + Ce	[116]				[116]	[116]		
	Ru + Mg	[107]				[107]			

Co	Al		[99]	[99]	
	Ni		[99]	Slight decrease [99]	
	Cu	[99]	[99]	[99]	
	Y		[103]	[103]	
	Zr		[104]	[104]	
	Ru		[102]	[102]	[102]
	Pd		[102]	[102]	[102]
	Ir		[102]	[102]	[102]
	Pt		[102]	[102]	[102]
Rh	Pt	[105]	[105]	CO selectivity [105]	

2.6 References

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3 Ni-based bimetallic catalysts for (sorption-enhanced) steam methane reforming

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Abstract

The catalytic performance of a monometallic Ni/Al₂O₃ and three bimetallic catalysts (Ni₃M₁/Al₂O₃, with M = Cu, Fe, and Ge) for the (sorption-enhanced) steam methane reforming reaction was evaluated. Ni₃Cu₁/Al₂O₃ was found to be the optimal catalyst in terms of methane conversion, hydrogen yield, and purity. Ge also has a promoting effect on the monometallic Ni catalyst, whereas the addition of Fe negatively influenced its performance. Physico-chemical characterization of the materials indicated the formation of alloys upon activation of the materials with hydrogen. The addition of Cu increased the surface area and metal dispersion, and improved the overall morphology of the catalyst. The experimental observations were also supported by a numerical study combining Density Functional Theory-based calculations and Microkinetic modelling of the SMR process. Ni₃Cu₁ and Ni₃Ge₁ were calculated to have a similar level of catalytic activity as Ni, whereas Ni₃Fe₁ was unsuitable for the reaction. The SMR reaction was further improved by adding calcium oxide as the CO₂ sorbent, which increased methane conversion, CO selectivity, hydrogen yield, and hydrogen purity. The highest methane conversion of 97% was achieved by Ni/Al₂O₃ and Ni₃Cu₁/Al₂O₃ at 700 °C.

Keywords:

Bimetallic catalyst, Hydrogen production, Steam methane reforming, Sorption-enhanced steam methane reforming, Microkinetic modelling

3.1 Introduction

Hydrogen is one of the most promising alternatives to fossil fuels for several industrial applications because of its clean combustion products and high-grade heat generated upon combustion. Currently, Steam Methane Reforming (SMR) is the most predominant industrial process used for hydrogen and syngas production. The SMR reaction takes place at high temperature and pressure (typically between 700 – 1000 °C and 14 – 20 bar [1]) in the presence of a catalyst and is accompanied by the Water-Gas Shift (WGS) reaction, which further enhances hydrogen production. Removal of the CO₂ produced in this process is usually carried out through in-process capture or endpoint capture using technologies like amine-based solvent scrubbing or Pressure Swing Adsorption [2]. In recent years, a novel technology – sorption-enhanced steam methane forming (SESMR) – has been proposed, which integrates *in-situ* CO₂ capture with the conventional SMR process. The integration of the CO₂ capture unit with the reforming reactor enhances hydrogen production by shifting the equilibrium of the reactions and reduces the overall cost of the system as a more compact process unit is employed [3].

Both SMR and SESMR require the presence of a catalyst to proceed at a sufficient rate. Commercial Ni-based catalysts are the most commonly used because of their high catalytic activity, good availability and relatively low price. However, some of the major issues associated with Ni-based materials include sintering, carbon deposition, and sulphur poisoning. The addition of a second metallic element to enhance the performance Ni-based catalysts has been extensively investigated, and noble metals (including Ru, Rh, Pd and Pt) have been found to be excellent promoters [4]. Although these materials have high catalytic activity and good stability, their application to industrial processes is limited by the cost of noble metals. Researchers have therefore turned to non-noble metal promoters and bimetallic catalysts in search of cost-effective

alternatives. Xu et al. [5] developed a microkinetic model based on the elementary reaction steps of SMR and screened a list of ~500 bimetallic alloys based on their adsorption energies, thermodynamic stability, oxide stability, and price. They concluded that Ni_3Fe_1 , Co_3Ni_1 , and Ni_3X_1 ($\text{X} = \text{Ge}, \text{As}, \text{and Sb}$) are potentially good candidates for SMR at high temperatures. A similar approach was employed by Liu et al. [6] to screen a large database containing 5,000 adsorption energies on different bimetallic surfaces and adsorption sites. They identified 48 stable and inexpensive bimetallic alloys that are potentially active for SMR, among which Ni_3Cu_1 , Ni_1Fe_1 , and Ni_3Co_1 are present.

Khazouzi et al. [7] tested the performance of a Ni-Cu/ Al_2O_3 catalyst for low temperature SMR and concluded that Cu acts as a stabilizer and improves the overall activity of the bimetallic material by inhibiting coke formation. Huang and Zhao [8] carried out SMR tests with samaria-doped ceria supported Ni-Cu catalyst and attributed the enhanced performance to the promoting effect of Cu to the WGS reaction. MgO supported Ni-Cu and Ni-Fe catalysts were tested for both steam and dry methane reforming by Djaidja et al. [9], results showed that although the addition of Cu and Fe decreased the overall catalytic activity, stability of the materials were improved with less carbon formation. On the other hand, very few studies have been carried out on Ni-Ge-based catalysts. Furukawa et al. [10] used Ni-Ge/ SiO_2 as the catalyst for hydrogen production from ammonia-borane and it exhibited higher catalytic activity compared to Ni/ SiO_2 . It is therefore of interest to investigate the performance of Ni-Ge-based bimetallic catalyst for SMR, as it has been predicted to have a high activity [5]. Although Ni-As and Ni-Sb alloys were also predicted to be active for SMR, they were excluded from this study due to the toxicity of As and Sb.

In this study, the catalytic performance of a monometallic Ni/ Al_2O_3 catalyst and a series of Ni-based bimetallic catalysts (noted $\text{Ni}_3\text{M}_1/\text{Al}_2\text{O}_3$, with $\text{M} = \text{Cu}, \text{Fe}, \text{and Ge}$) were evaluated and compared. The materials were then tested under both SMR and SESMR conditions, and their catalytic activity was further evaluated with ab-initio Density Functional Theory (DFT)-based simulations and Microkinetic modelling (MKM). This combined experimental and numerical study of bimetallic catalysts provides insight into the promoting effect of several widely

available non noble metals and their potential as novel alternatives to the conventional Ni-based material. This work also aims to provide an experimental verification of previous high-throughput screening studies and is also the first ever attempt to experimentally test Ni-Ge-based material as an SMR catalyst.

3.2 Methodology

3.2.1 Catalyst synthesis

Ni/Al₂O₃, Ni₃Cu₁/Al₂O₃ and Ni₃Fe₁/Al₂O₃ catalysts were synthesized by impregnating the alumina support (gamma-phase, bimodal, Alfa Aesar) with the aqueous solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99%, Thermo Scientific Chemicals), copper nitrate hemi-pentahydrate (Cu(NO₃)₂·2.5H₂O, 98%, Thermo Scientific Chemicals) and iron nitrate nonahydrate (Fe(NO₃)₉·9H₂O, 99%, Thermo Scientific Chemicals). Appropriate amount of metal precursors was dissolved in deionised water so that the total metal loading in the reduced samples was equal to 10 wt.%, and the Ni:Cu or Ni:Fe molar ratio was equal to 3:1. Ni₃Ge₁/Al₂O₃ was synthesized by impregnating the alumina support and GeO₂ powder (Germanium (IV) oxide, 99.9999%, Thermo Scientific Chemicals) with appropriate amount of nickel nitrate solution, so that the total metal loading in the reduced samples was equal to 10 wt.%, and the Ni:Ge molar ratio was equal to 3:1.

The solutions were then agitated in an ultrasonic tank for 3 hours at 60 °C and dried in a static oven overnight. The samples were then calcined at 500 °C for 4 h with a heating rate of 5 °C/min, followed by hydrogen reduction at 600 °C (Ni/Al₂O₃ and Ni₃Cu₁/Al₂O₃) or 800 °C (Ni₃Fe₁/Al₂O₃ and Ni₃Ge₁/Al₂O₃). A schematic diagram summarizing the key steps in the synthesis process and pictures of the Ni₃Cu₁/Al₂O₃ catalyst are presented in Figure 3-1 and Figure 3-2.

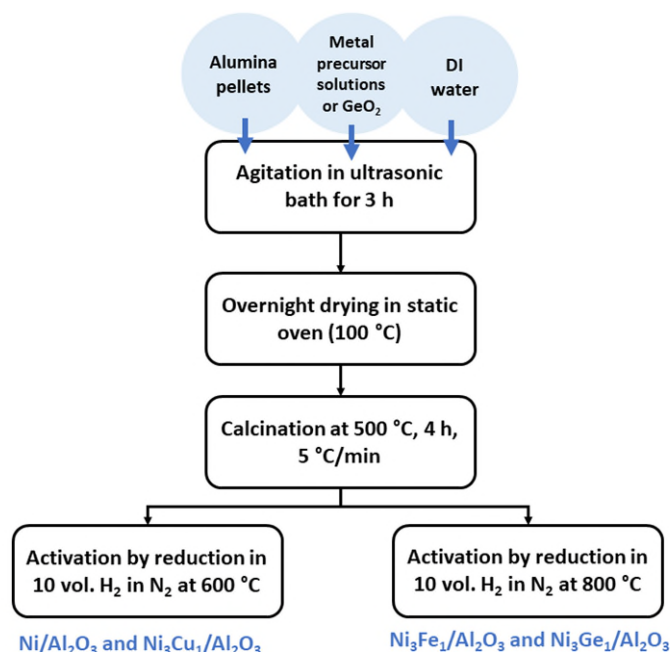


Figure 3-1 Schematic diagram of the synthesis process for the mono and bimetallic catalysts.



Figure 3-2 Pictures of the $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ catalyst (from left to right: after impregnation, after overnight drying, after calcination, and after reduction).

3.2.2 Characterization

The catalysts were characterized using different techniques, including X-ray fluorescence spectroscopy (XRF), Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX), N_2 physisorption, H_2 pulse chemisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Thermogravimetric analysis (TGA).

XRF analysis was carried out using a micro-XRF Bruker M6 Jetstream. Quantification was done using Fundamental parameters, with data acquired at 30 kV and 600 μ A.

SEM-EDX analysis was carried out using the TESCAN VEGA 3 scanning electron microscope.

N₂ adsorption and desorption isotherms were obtained using the Micromeritics 3 Flex instrument. Prior to the physisorption tests, the samples were degassed at 400 °C for 5 h with a heating rate of 10 °C/min to remove any moisture or impurities. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation, and the total pore volume and median pore radius were obtained from the Barrett-Joyner-Halenda (BJH) method.

A Micromeritics 3Flex was also used to perform pulse H₂ pulse chemisorption tests. Prior to the chemisorption measurements, pure hydrogen stream was flowed over one gram of fresh catalyst for 30 minutes to fully reduce the catalyst. The samples were then degassed in a N₂ stream and cooled down to 30 °C. Loop H₂ gas was pulsed over the sample for 10 times or until the area of the peaks was stable, indicating no further adsorption of H₂ by the sample.

XRD results were obtained with the Siemens D5005 X-ray Diffractometer using Cu K α radiation. The reduced samples were crushed into a powder and scanned in the 2 θ range of 30° – 80° with a step size of 0.02°.

XPS analysis was carried out using a Thermofisher ESCALAB 250 electron spectrometer, which featured a hemispherical sector energy analyser. An Al K α X-ray source with a single energy level was employed to optimise resolution. The experiments maintained a source excitation energy of 15 KeV, an emission current of 6 mA, an analyser pass energy of 20 eV, a step size of 0.1 eV, and a dwell time of 50 ms. Throughout the examinations, the spectrometer consistently maintained a base pressure better than 5×10^{-10} mbar, ensuring that all recorded signals were originated from the sample surface.

TGA of the used catalysts was carried out using a Perkin Elmer TGA 8000. Prior to the TGA tests, all samples were reduced by hydrogen and degassed for 24 h to ensure no metal oxides or impurities were present. Approximately 20 mg of

sample was oxidized in air while being heated from 30 to 1000 °C with a heating rate of 10 °C/min. The change in sample weight during the oxidation process is equal to difference between the weight loss due to carbon combustion, and the weight increase due to metal oxidation. The degree of carbon formation is evaluated using the following equation:

$$m_{\text{initial}} + m_{\text{oxidation}} - m_{\text{carbon}} = m_{\text{final}} \quad \mathbf{3-1}$$

$$\text{carbon amount (wt. \%)} = \frac{m_{\text{carbon}}}{m_{\text{initial}}} \quad \mathbf{3-2}$$

Where m_{initial} is the initial weight of the sample used for TGA, m_{final} is the final weight of the sample after TGA, $m_{\text{oxidation}}$ is the weight gained due the oxidation of metal in the air flow, and m_{carbon} is the weight reduced due to the combustion of carbon. Both m_{initial} and m_{final} were measured directly by the balance of the TGA instrument. $m_{\text{oxidation}}$ was calculated using results from the XRF analysis (to determine the weight of each metal in the sample) and by assuming that all active metals (Ni, Cu, Fe, and Ge) are fully oxidised by the end of the TGA test. The carbon amount is defined as the amount of carbon present in the sample.

TGA of the used sorbent from the SESMR tests (with $T = 700\text{ }^{\circ}\text{C}$) was also carried out to determine the amount of coke deposited on the sorbent material. Samples of used sorbent were heated from $30\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ in air flow with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The TGA test of used sorbent consists of three main mass loss stages, which is considered to be typical for air TGA test of calcium oxide powders with coke deposition [11]. The first mass loss stage between $100 - 150\text{ }^{\circ}\text{C}$ is due to the release of moisture. The second stage at around $450\text{ }^{\circ}\text{C}$ is due to the decomposition of $\text{Ca}(\text{OH})_2$, the sample weight by the end of this stage is noted m_1 . The final stage between $600 - 700\text{ }^{\circ}\text{C}$ is due to the combustion of deposited coke, and the sample weight by the end of this stage is noted m_2 .

The amount of carbon deposited on the sorbent is calculated using the equation below:

$$m_{\text{carbon}}(\text{wt. \%}) = \frac{m_1 - m_2}{m_1} \quad \text{3-3}$$

A more intuitive visual representation of the TGA curves with numerical values can be found in section

3.2.3 Activity test

A fixed bed reactor described by Shen et al. [12] was used to test the catalytic activities of $\text{Ni}/\text{Al}_2\text{O}_3$, $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$, $\text{Ni}_3\text{Fe}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ catalysts under SMR and SESMR conditions. The Process Flow Diagram of the reactor system is shown in Figure 3-3. A 10 vol.% CH_4/N_2 gas cylinder (BOC UK) was connected to the main fixed-bed reactor and was used as the feed stream for both SMR and SESMR. A 10 vol.% H_2/N_2 cylinder (BOC UK) was also connected to the reactor for the activation of the catalysts prior to the reforming tests. The gases were introduced into the main reactor with mass flow controllers (Bronkhurst UK). A steam generator provided steam for the reactor (using nitrogen as carrier gas) and its flow rate was controlled by an HPLC pump (Jasco PU1586). The main reactor consisted of a quartz liner with an inner diameter of 2 cm. The catalysts and sorbents were fixed in the centre of the quartz liner with two layers of quartz wool. The bed temperature of the reactor was monitored by a K-type thermocouple. The outlet gas stream was cooled down by a water-cooled condenser and passed through a tube packed with CaCl_2 , where moisture was absorbed. The composition of the dried gas was then measured and recorded by two multi-gas analysers (ADC MGA3000).

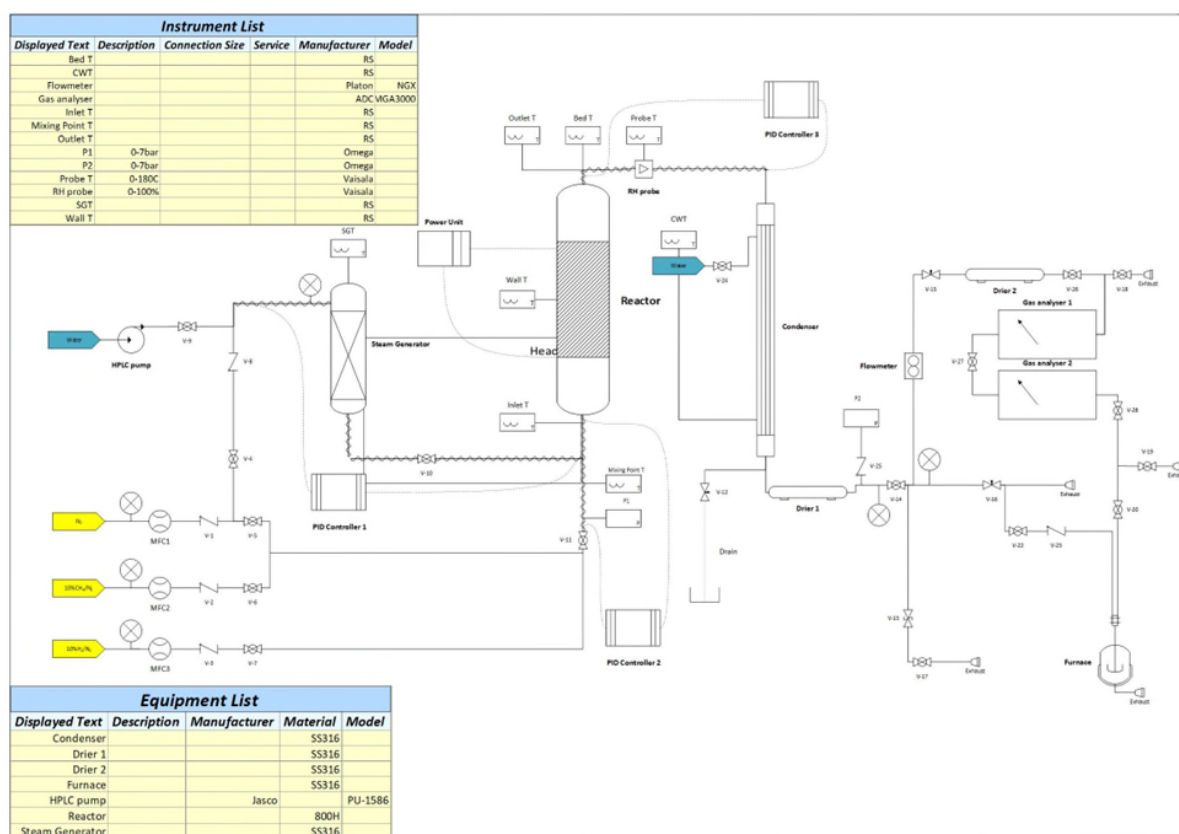


Figure 3-3 Process Flow Diagram of the reactor system.

3.2.3.1 Catalytic activity test for SMR

Approximately 2.5 g of catalysts was introduced at the centre of the reactor. The catalysts were reduced under a fixed gas flow of 10% hydrogen (balanced with nitrogen) under 600 °C until no water was observed by the humidity probe (Vaisala HMT330 series) in the exhaust gas line. A gaseous feedstock of 10 vol.% methane in nitrogen was then passed through the fed after a stable water content was generated in the system through an HPLC pump (Jasco, model PU1586). The operating temperatures of catalyst activity tests were controlled, ranging from 600 °C to 800 °C. The exhaust gases were analysed to determine the actual gas composition in a dry basis via a bundle of gas analysers (ADC MGA3000 model). All tests were carried out under atmospheric pressure, while a gas hourly space velocity (GHSV) of 15,000 h⁻¹ was chosen.

3.2.3.2 Catalytic activity test for SESMR

For SESMR, limestone (Longcliffe) was selected to be the sorbent material. The limestone was sieved to control the particle size to be in the range of 315 to 400 microns. In a typical SESMR test, approximately 3 g of sorbent was mixed with 2.5 g of catalysts and then the mixture was placed in the middle of the reactor using a quartz liner. The materials were sufficiently vibrated so that better contact could be achieved between the catalyst pellets and the sorbent particles. The catalyst/sorbent mixture was activated under the same hydrogen flow for SMR but at 850 °C. The mixture was considered to be fully activated when there was no water generation and no carbon dioxide was detected, which indicates the complete reduction of the catalyst and the complete calcination of the limestone. The SESMR tests were carried out at 600, 650, and 700 °C, as CO₂ adsorption occurs at temperatures lower than 760 °C [13], and the process shifts from SESMR to the conventional SMR at higher temperatures. Methane conversion, hydrogen yield, hydrogen purity, and CO selectivity were calculated based on the pre-breakthrough stage [14], and the averaged data are presented in this paper. Because of the sorbent, a lower operating temperature was chosen, which was controlled to be between 600 and 700 °C. The sorbent was disposed of after each test and for each SESMR test, only one temperature was selected. The same GHSV and pressure as the SMR tests were applied for all SESMR tests.

With the gas composition data collected, methane conversion, hydrogen yield, hydrogen purity and carbon monoxide selectivity were determined via equations below:

$$\text{CH}_4 \text{ conversion} = \frac{\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out}}{\text{CH}_4 \text{ in}} \quad \text{3-4}$$

$$\text{H}_2 \text{ yield} = \frac{4 \times \text{H}_2 \text{ out}}{\text{CH}_4 \text{ in}} \quad \text{3-5}$$

$$\text{H}_2 \text{ purity} = \frac{\text{H}_2 \text{ out}}{\text{CH}_4 \text{ out} + \text{H}_2 \text{ out} + \text{CO out} + \text{CO}_2 \text{ out}} \quad \text{3-6}$$

$$\text{CO selectivity} = \frac{\text{CO out}}{\text{CO out} + \text{CO}_2 \text{ out}} \quad \text{3-7}$$

Methane conversion under thermodynamic equilibrium conditions was obtained using FactSage software. FactSage equilibrium calculation was carried out under batch conditions. The same conditions as the experimental SMR tests were used: atmospheric pressure, steam to carbon ratio of 3 and temperatures of 600, 700 and 800 °C. However, it should be noted that FactSage can only simulate the gas compositions thermodynamically, assuming no influence or presence of catalysts/sorbent and the materials were perfectly mixed.

3.2.4 Density Functional Theory

All DFT-based calculations in this work were carried out using the Quantum Espresso software package [15]. The projector augmented wave (PAW) method [16] was used to simulate the interactions between the electrons and the ions. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used to describe the exchange correlation [17]. The plane wave cutoff energy was set to be 400 eV. A Monkhorst-Pack $3 \times 3 \times 1$ k-point grid was used to sample the Brillouin zone. Spin polarization effects were taken into account for magnetic elements. The convergence criteria for force and energy were set to be 0.025 eV/Å and 10^{-5} eV, respectively. All catalysts were simulated by a four-layer $p(2 \times 2)$ slab model, with the top two layers and the adsorbate relaxed, and the bottom two layers fixed. The two neighbouring layers in the z-direction were separated by a 10 Å vacuum. The adsorption energy, E_{ads} , is calculated as below:

$$E_{\text{ads}} = E_{\text{ads*slab}} - E_{\text{ads}} - E_{\text{slab}}$$

Where $E_{ads*slab}$ is the total energy of the slab with the adsorbate, E_{ads} is the total energy of the isolated phase adsorbate, and E_{slab} is the total energy of the clean slab.

All gas phase species were modelled by placing the molecule in a cube with the lattice parameters of $a = 20 \text{ \AA}$, $b = 20.5 \text{ \AA}$, $c = 21 \text{ \AA}$. A Monkhorst-Pack $1 \times 1 \times 1$ k-point grid was used to sample the Brillouin zone.

3.2.5 Microkinetic modelling

The microkinetic model was implemented using the descriptor-based analysis package CatMAP [18]. The model was constructed using the elementary steps of the SMR reaction, and reaction energetics obtained from DFT calculations, combined with the unity bond index-quadratic exponential potential (UBI-QEP) method and the Brønsted–Evans–Polanyi (BEP) relationship. The model was built based on the adsorption on 7 transition metal surfaces, including Rh(111), Ni(111), Cu(111), Fe(110), Pd(111), Pt(111), and Au(111). Detailed information on the reaction steps and energetics can be found in Supplementary Information (Appendix B.2).

3.3 Results and discussion

3.3.1 Characterization

3.3.1.1 XRF analysis

The XRF analysis was carried out to determine the actual metal loading and Ni:M ratio of the samples (Table 3-1). The actual metal loading of all samples is very close to the theoretical value of 10%, with errors less than 6.3%. The Ni:Cu and Ni:Ge ratios were measured to be 2.69 : 1 and 2.7 : 1, which are close to the theoretical value of 3 : 1. However, the measured Ni:Fe ratio is significantly lower than the theoretical value. This agrees with the observation during the catalyst synthesis process – nickel nitrate has a higher water solubility compared with iron nitrate, making it easier to thoroughly penetrate the alumina pellets in the liquid form during the heated agitation process. As XRF is a surface technology, Fe

segregated on the outer layer of the support resulted in a higher iron concentration.

Table 3-1 Theoretical and measured total metal loading and Ni:M ratio.

	Total metal loading (wt.%)		Ni:M ratio	
	Theoretical	Measured	Theoretical	Measured
Ni/Al ₂ O ₃		9.88	-	-
Ni ₃ Cu ₁ /Al ₂ O ₃	10	10.02	3 : 1	2.79 : 1
Ni ₃ Fe ₁ /Al ₂ O ₃		9.37	3 : 1	2.01 : 1
Ni ₃ Ge ₁ /Al ₂ O ₃		10.58	3 : 1	2.67 : 1

3.3.1.2 SEM-EDX analysis

Prior to the SEM-EDX analysis, the cylindrical catalyst pellets were cut in half, and the SEM images of the inner section of the fresh calcined catalysts are presented in Figure 3-4. The alumina support consists of interconnecting pores which allows for the efficient diffusion of reaction gases. All catalysts exhibit very similar morphological features, with a uniform distribution of metal particles on the support. The size of the particles is in the range of 5 – 30 μm . The spatial distribution of the active metals within the support was evaluated using EDX. The elemental mapping and the composition of the scanned area are presented in Figure 3-5. It is evidenced that for all samples, the active metals are evenly distributed within the support with no apparent phase segregation or agglomeration. Cu and Ge were dispersed within the support with the desired ratio, meaning that a uniform layer of bimetallic species has been formed. However, it should be noted that the Ni:Fe ratio at the inner section of the Ni₃Fe₁/Al₂O₃ sample is lower than the theoretical value of 3 : 1 (Figure 3-5 (c)). This is consistent with the observation stated in section 3.3.1.1 that Ni penetrates the alumina support more easily compared with Fe, and therefore is more evenly distributed.

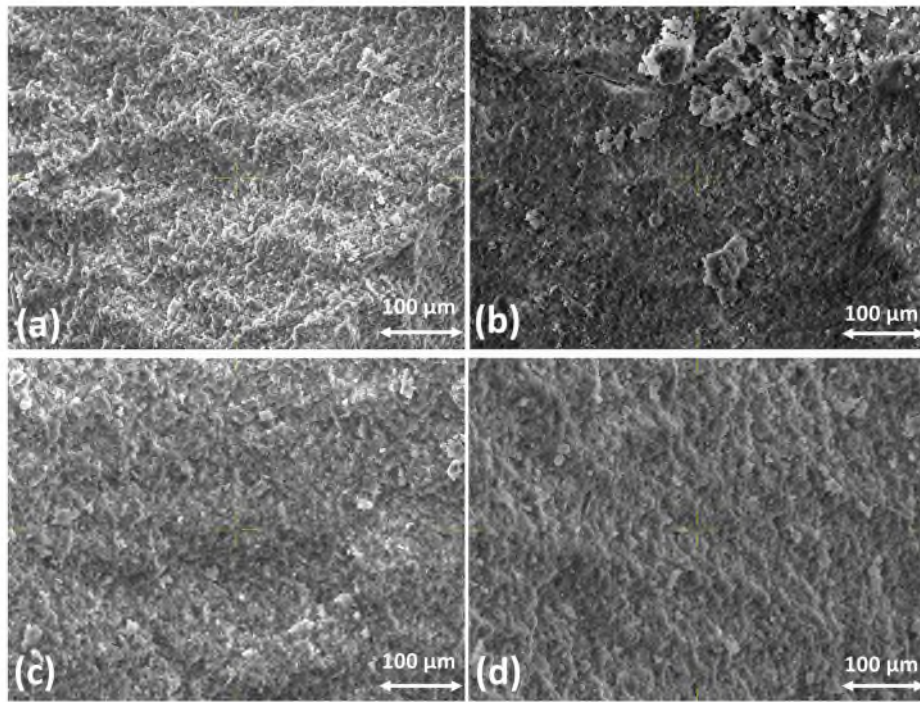


Figure 3-4 SEM images of (a) Ni/Al₂O₃, (b) Ni₃Cu₁/Al₂O₃, (c) Ni₃Fe₁/Al₂O₃, (d) Ni₃Ge₁/Al₂O₃.

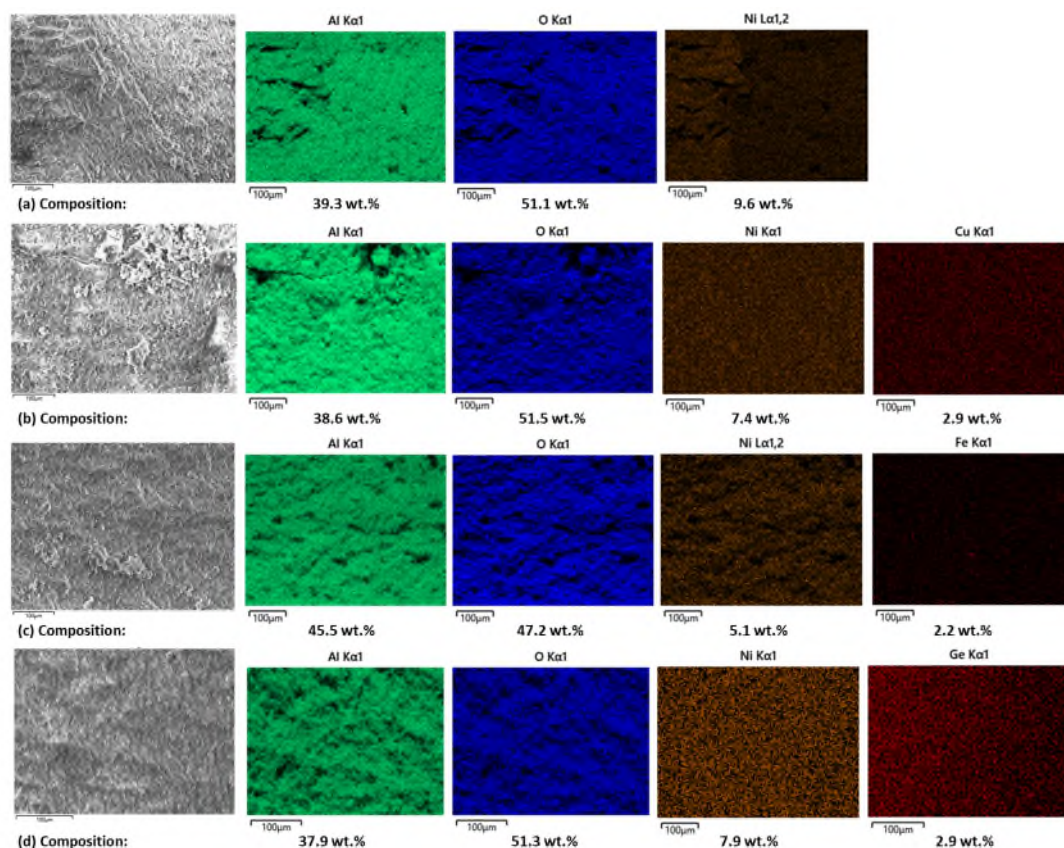


Figure 3-5 EDX elemental mapping of (a) Ni/Al₂O₃, (b) Ni₃Cu₁/Al₂O₃, (c) Ni₃Fe₁/Al₂O₃, (d) Ni₃Ge₁/Al₂O₃.

3.3.1.3 N₂ physisorption

The results obtained from the N₂ physisorption analysis are summarised in Table 3-2. The untreated alumina support has a BET surface area of 227.2 m²/g, a BJH pore volume of 0.77 cm³/g and a median pore diameter of 12.2 nm. The metal loaded fresh samples have smaller surface area and pore volume compared to the bare support, as the metal particles may block the pores of alumina during the impregnation process [19]. The surface area, pore volume, and pore size were slightly increased after the reduction process. The BJH analysis indicated that the catalysts are mesoporous, with median pore diameters in the range of 10 – 14 and 12 – 15 nm for the fresh and reduced samples, respectively. Among the bimetallic catalysts, Ni₃Cu₁/Al₂O₃ showed a higher surface area compared with the monometallic Ni catalyst. This promoting effect of Cu to the overall textural properties of the bimetallic catalyst was also observed by Khzouz et al. [7], and

is attributed to the more uniform distribution of the metallic species on the support surface and less blockage of pores.

Table 3-2 Results from N₂ physisorption analysis.

	BET surface area (m ² /g)		BJH adsorption pore volume (cm ³ /g)		BJH adsorption median pore diameter (nm)	
Alumina	227.16		0.77		12.22	
	Fresh	Reduced	Fresh	Reduced	Fresh	Reduced
Ni/Al ₂ O ₃	190.3	227.7	0.62	0.77	11.96	12.37
Ni ₃ Cu ₁ /Al ₂ O ₃	217.0	222.5	0.69	0.77	11.50	12.56
Ni ₃ Fe ₁ /Al ₂ O ₃	176.3	180.7	0.62	0.70	13.35	14.30
Ni ₃ Ge ₁ /Al ₂ O ₃	179.5	159.6	0.52	0.58	10.84	13.61

3.3.1.4 H₂ chemisorption

The hydrogen uptake amount, metal dispersion rate, metallic surface area, and crystallite size of the catalysts obtained by H₂ chemisorption analysis are summarized in Table 3-3. The highest H₂ uptake amount was obtained by Ni/Al₂O₃ with a metal dispersion rate of 1.07%, which is on a similar level as other alumina-supported Ni catalysts synthesized by the wet-impregnation method [20]. Compared with Ni/Al₂O₃, all bimetallic catalysts showed a lower H₂ uptake amount. The dilution of surface Ni atoms by the addition of the second element and possible formation of bimetallic alloys decreased the H₂ uptake amount and the metallic surface area of Ni. This is consistent with the results reported in literature, where the dispersion rate of the main active metal is decreased when Cu [21], Fe [22] or Ge [23] is added. It is also observed that the addition of Cu and Fe decreased the crystallite size of the bimetallic catalysts, whereas Ge significantly increased it.

Table 3-3 Results from H₂ pulse chemisorption tests.

	H ₂	Metal	Metallic surface area		Crystallite size (Å)
	uptake (μmol/g)	dispersion (%)	m ² /g sample	m ² /g metal	
Ni/Al ₂ O ₃	14.04	1.07	0.56	5.56	1,010.3
Ni ₃ Cu ₁ /Al ₂ O ₃	9.43	1.56	0.37	5.33	505.4
Ni ₃ Fe ₁ /Al ₂ O ₃	8.14	0.62	0.41	4.07	410.4
Ni ₃ Ge ₁ /Al ₂ O ₃	5.21	0.42	0.25	2.48	2,940.5

3.3.1.5 XRD analysis

The XRD patterns of the reduced samples with a zoom of the peaks in the range of 40° – 55° are presented in Figure 3-6, and the peaks were fitted using the Inorganic Crystal Structure Database [24]. No crystallite peaks were detected for the bare alumina support, indicating that the alumina used was amorphous, which is not unexpected [25,26]. In Figure 3-6 (b), the dashed lines indicate the positions of the (111) and (200) reflections of pure Ni. The peaks with the highest intensity located at 44.25°, 44.21°, and 43.53° were assigned to the (111) peaks of the Ni₃Cu₁, Ni₃Fe₁, and Ni₃Ge₁ solid solutions, respectively. The peaks with lower intensity between 50° – 52° and 74° – 76° correspond to the (200) and (220) surfaces of the face centred cubic bimetallic alloys. The shift of the peaks to lower angles compared with pure Ni confirmed the formation of bimetallic alloys and also indicates an increase in the lattice size of the alloys compared with pure Ni [27]. The lattice constant of Ni₃Cu₁, Ni₃Fe₁, and Ni₃Ge₁ were estimated using Bragg's Law, and were calculated to be 3.538, 3.541, and 3.577 Å, respectively. No other peaks with low intensities were identified, showing the high crystallinity and phase purity of the alloy formed after the reduction process [28].

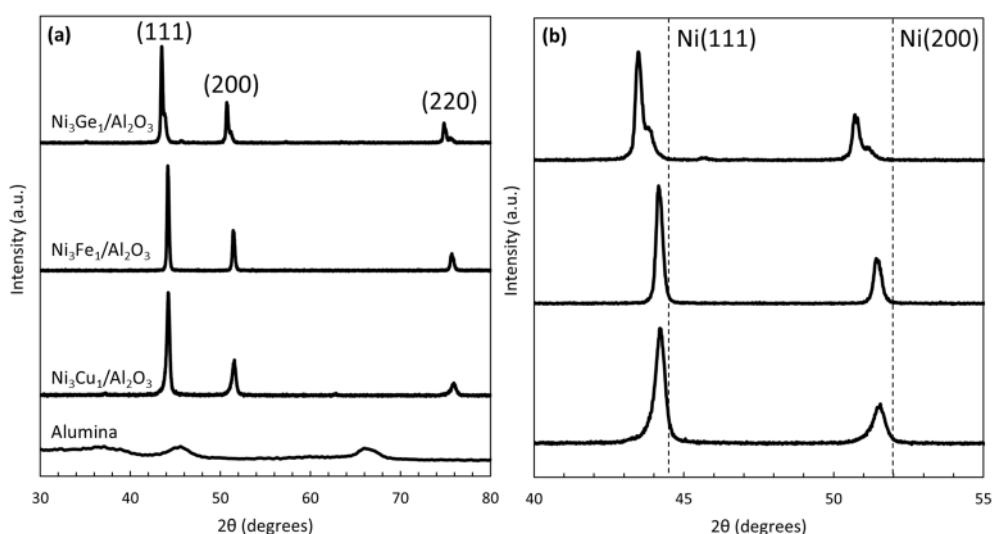


Figure 3-6 XRD patterns of the alumina support and the reduced bimetallic catalysts: (a) overall pattern (b) a zoom of the 2θ range of $40^\circ - 55^\circ$.

3.3.1.6 XPS analysis

The surface state of the reduced samples was examined using XPS analysis, and the spectra obtained are presented in Figure 3-7. In Figure 3-7 (a), the 2p $3/2$ peaks at 852.6 and 856.2 eV are attributed to metallic Ni^0 and NiO (Ni^{2+}), respectively. The 2p $1/2$ peak at 873.6 eV was attributed to NiO (Ni^{2+}). Weaker satellite peaks were observed at the higher binding energy side of the two main peaks (861.8 and 880.6 eV), which is a typical characteristic of nickel [29]. The same main peaks and their corresponding satellite peaks were also observed for two of the bimetallic catalysts (Figure 3-7 (b) and (c)). However, the peaks are slightly shifted towards to higher binding energy side, which is possibly due to their strong interaction with the alumina support [30]. For $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$, the peaks at 854.1 and 871.7 eV are attributed to $\text{Ni}(\text{OH})_2$ (Ni^{2+}). In the Cu 2p spectrum, the peaks at 934.4 and 954 eV correspond to CuO (Cu^{2+}) 2p $3/2$ and Cu^0 2p $1/2$, respectively [31,32]. The Fe 2p spectrum contains three main peaks with relatively low intensity at 707, 711.5 and 724.8 eV, which correspond to Fe^0 2p $3/2$, a combination of Fe^{2+} 2p $3/2$ and Fe^{3+} 2p $3/2$, and a combination of Fe^{2+} 2p $1/2$ and Fe^{3+} 2p $1/2$ [33,34]. Finally, two peaks at 1222 and 1253 eV were observed in the Ge 2p spectrum, corresponding to GeO_2 (Ge^{4+}) 2p $3/2$ and GeO_2 (Ge^{4+}) 2p $1/2$ [35]. It has been observed that metal oxides were present in all of

the reduced samples, which is mainly due to the inevitable oxidation by air during storage and transportation of the samples.

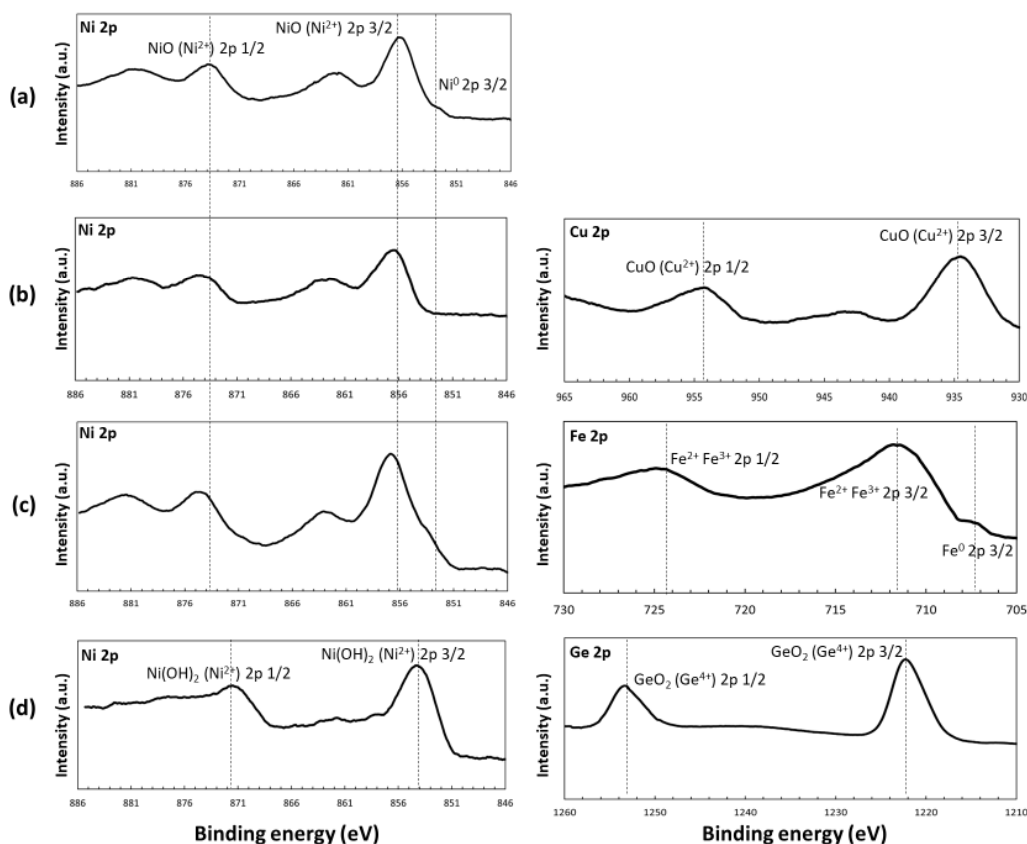


Figure 3-7 XPS spectra of reduced (a) Ni/Al₂O₃, (b) Ni₃Cu₁/Al₂O₃, (c) Ni₃Fe₁/Al₂O₃, (d) Ni₃Ge₁/Al₂O₃.

3.3.2 Catalytic performance study for steam methane reforming

The catalytic performance of Ni/Al₂O₃ and the bimetallic catalysts for the SMR reaction was evaluated based on the CH₄ conversion, H₂ yield and purity, as well as the CO selectivity. To evaluate the repeatability of the experiments, SMR tests using Ni₃Cu₁/Al₂O₃ were repeated three times at 600, 700 and 800 °C, and the standard deviation error bars of each set of results was plotted in Figure 3-8.

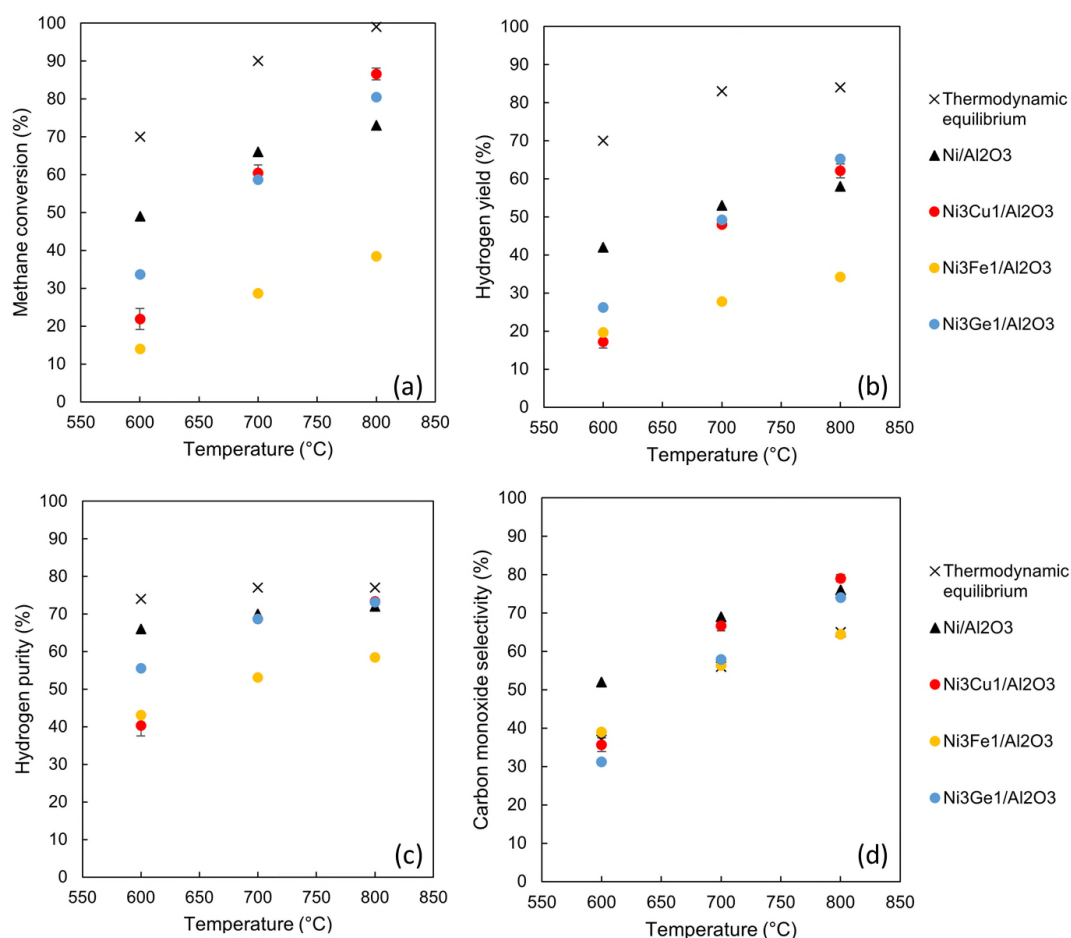


Figure 3-8 (a) Methane conversion, (b) hydrogen yield, (c) hydrogen purity, and (d) CO selectivity of the mono and bimetallic catalysts under SMR conditions.

All catalysts showed an increase in methane conversion with higher reaction temperature, as the SMR reaction is endothermic. The promoting effect of Ge and Cu becomes increasingly significant as reaction temperature rises, with the highest methane conversion of 87% achieved by Ni₃Cu₁/Al₂O₃ at 800 °C. The difference between the methane conversion level at thermodynamic equilibrium and the measured values is potentially due to the high GHSV (15,000 h⁻¹) used and the low methane concentration (10 vol.%) in the feed stream, which decreased the possibility of contact between the reaction gases and the catalyst. Similar to Cu, Ge enhanced the catalytic activity of Ni catalyst at 800 °C with a methane conversion rate of 80%. A similar trend was observed for hydrogen yield and hydrogen purity – both values increase as temperature rises. Compared with the monometallic Ni catalyst, Ni₃Cu₁/Al₂O₃ and Ni₃Ge₁/Al₂O₃ showed higher

hydrogen yield and purity at higher temperatures, with a maximum value of 64% and 72%, respectively.

It is generally agreed that noble metals are the most active for SMR – Ru-, Rh-, Pt-, and Pd-promoted Ni catalysts were reported to be able to achieve a methane conversion same to the thermodynamic equilibrium level [36–38]. Although the methane conversion of $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ are 10 – 15% lower compared with the noble metal-promoted catalysts, it should be noted that Cu and Ge are much more available and cost-effective compared to noble metals.

CO selectivity serves as a measurement of the extent of the WGS reaction within the system. The WGS reaction allows for the production of more hydrogen through the conversion of CO and H_2O . As shown in Figure 3-8 (d), the CO selectivity of $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ was on a similar or lower level compared with $\text{Ni}/\text{Al}_2\text{O}_3$. In particular, both $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ showed a higher methane conversion rate with a lower CO selectivity at 800 °C. This indicates that the addition of Cu and Ge improved the activity of the catalysts by enhancing the WGS reaction, the methane consumed by the SMR reaction was therefore further converted to CO_2 through WGS, leading to a low CO selectivity.

On the other hand, the addition of Fe has a significant negative impact on the activity of the catalyst, which is in contraction to the predictive results reported by Xu et al. [5]. This is partially due to the morphological properties of $\text{Ni}_3\text{Fe}_1/\text{Al}_2\text{O}_3$ – as shown by both XRF and SEM-EDX analysis, Fe particles tend to segregate on the surface of the alumina support, which may lead to blockage of surface pores, leaving insufficient entrance for reactant gases to enter the support. Ni-Fe alloy also requires a relatively high reduction temperature, which is between 600 – 800 °C based on previous literature [39,40]. This may have led to an incomplete activation of the $\text{Ni}_3\text{Fe}_1/\text{Al}_2\text{O}_3$ catalyst prior to the SMR test, as results from the XPS analysis evidenced the presence of iron oxide species within the reduced sample. To further explore how the addition of Cu, Fe and Ge influences the performance of the nickel catalyst, a series of first principle-based calculations

and microkinetic modelling were carried out, and the results are presented in section 3.3.4.

The used catalysts were characterized using N₂ physisorption and TGA, and the results are summarized in Table 3-4. Once subjected to the approximately 1.5-hour SMR test (with reaction temperature continuously varying from 600 to 800 °C), the surface area and pore volume of the catalysts were decreased with an increase in pore diameter. This is as expected, due to the potential sintering of the active metals and pore blockage by coke at higher temperatures. All bimetallic catalysts showed a better carbon resistant ability compared with the monometallic Ni/Al₂O₃, with the lowest carbon formation amount of 2.26% achieved by Ni₃Cu₁/Al₂O₃. The enhanced stability of the bimetallic catalysts may be achieved due to the formation of Ni-based alloys (as indicated by the XRD results in section 3.3.1.5.), which prevented the formation of bulk Ni particles prone to coke formation [9].

Table 3-4 Properties of the used catalysts after SMR tests.

	BET surface area (m ² /g)	BJH adsorption pore volume (cm ³ /g)	BJH adsorption median pore diameter (nm)	Carbon amount (wt.%)
Ni/Al ₂ O ₃	180.9	0.65	12.37	3.37
Ni ₃ Cu ₁ /Al ₂ O ₃	192.4	0.76	14.46	2.26
Ni ₃ Fe ₁ /Al ₂ O ₃	164.7	0.65	14.74	2.98
Ni ₃ Ge ₁ /Al ₂ O ₃	163.7	0.58	13.62	3.29

3.3.3 Catalytic performance study for sorption-enhanced steam methane reforming

The catalytic performance of Ni/Al₂O₃ and the bimetallic catalysts was also evaluated under SESMR conditions at 600, 650 and 700 °C, and the results are presented in Figure 3-9. Figure 3-10 presents the composition of the outlet gas stream of the SESMR test at 700 °C using Ni/Al₂O₃ as the catalyst. The

concentration of CO₂ in the outlet gas stream at 700 °C was approximately 2 vol.% (corresponding to a CO selectivity of ~73%). The outlet CO₂ concentration can be further decreased by reducing the GHSV of the system to increase the contact time between CO₂ and the sorbent, or by reducing the particle size of the sorbent [41].

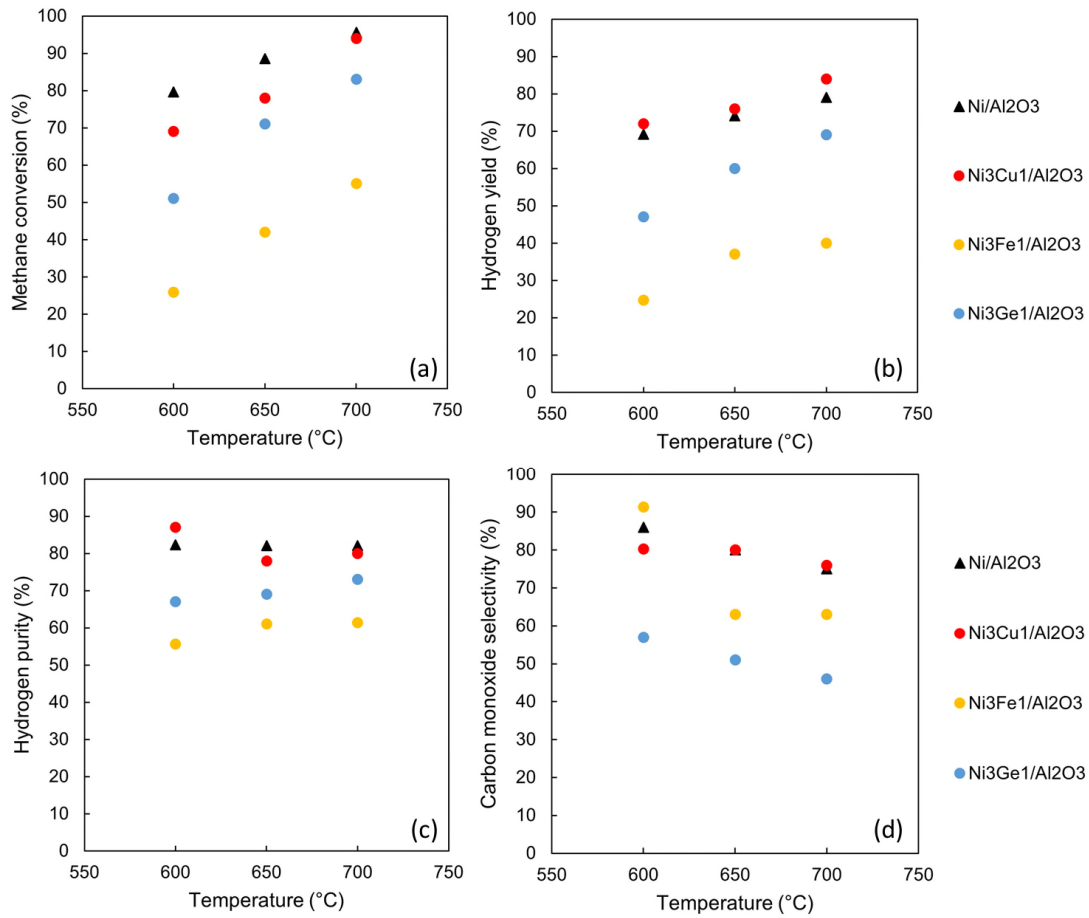


Figure 3-9 (a) Methane conversion, (b) hydrogen yield, (c) hydrogen purity, and (d) CO selectivity of mono and bimetallic catalysts under SESMR conditions.

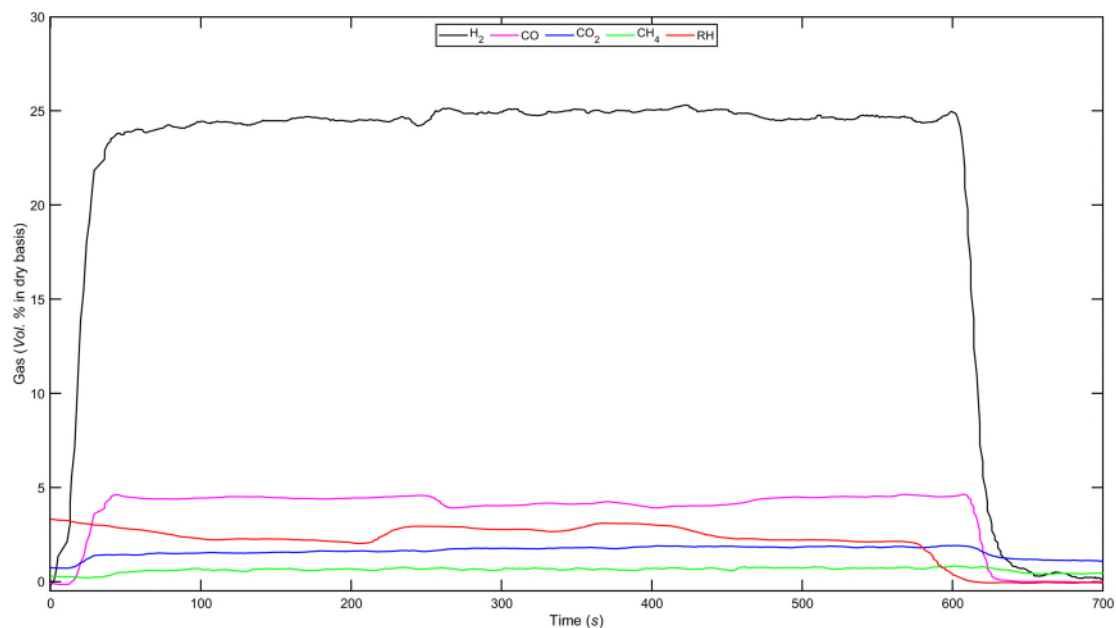


Figure 3-10 Composition of the outlet gas stream for SESMR at 700 °C (using Ni/Al₂O₃ as catalyst).

By increasing the reaction temperature from 600 to 700 °C, both methane conversion and hydrogen yield were improved. This was attributed to the enhancement of the endothermic SMR reaction, while in the meantime, the adverse effect of high temperature on the exothermic WGS and CO₂ adsorption reactions was not as significant. Compared with the SMR test under the same reaction temperature ($T = 700\text{ °C}$), the addition of the CO₂ sorbent improved the methane conversion of all catalysts by approximately 20 – 30%. The highest methane conversion rate of 95% was achieved by Ni/Al₂O₃ and Ni₃Cu₁/Al₂O₃ at 700 °C. Similarly, hydrogen yield, hydrogen purity, and CO selectivity were all enhanced in the presence of the sorbent. The sorbent in the system effectively absorbs the CO₂ produced through the WGS reaction, and therefore moves the reaction equilibrium towards the direction of hydrogen production. However, it should be noted that CO₂ absorption by calcium oxide is exothermic, a further increase in temperature will result in the process returning to its conventional SMR state. It is concluded that for the bimetallic catalysts focused on in this study, 700 °C is the optimal temperature for the materials to achieve the best performance, in terms of highest methane conversion, hydrogen yield and purity.

Compared with the tests under SMR conditions, the promoting effect of Ge is not as significant under SESMR conditions. Methane conversion, hydrogen yield and hydrogen purity of $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ were found to be lower than the monometallic $\text{Ni}/\text{Al}_2\text{O}_3$. It is also observed that $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ exhibited the lowest CO selectivity, meaning that CO_2 has not been effectively absorbed in the system. TGA tests of used sorbent from the SESMR tests at 700 °C were carried out and the TGA curves are shown in Figure 3-11. The amount of carbon deposited on the used sorbent from the four tests was calculated to be 4.68 wt.%, 6.07 wt.%, 6.06 wt.%, and 6.80 wt.%, respectively (using Equation **Error! Reference source not found.**). It was observed that the amount of deposited carbon for the three tests using bimetallic catalysts was higher than that observed in the test using monometallic Ni. This is potentially due to the high carbon resistance of the three bimetallic catalysts, as demonstrated in 3.3.2, making elemental carbon more likely to be deposited on the surface of the calcium oxide sorbent. The relatively low CO selectivity of $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ was therefore attributed to the highest carbon deposition amount on the sorbent surfaces during the reaction – although sufficient steam-to-carbon ratio was utilised for the reaction, a relatively large amount of carbon in the feed was converted into coke instead of CO through side reactions, such as methane cracking or the Boudouard reaction [42]. The carbon formed was deposited on the surface of the calcium oxide sorbent, reducing its ability to effectively absorb the CO_2 formed by the WGS reaction.

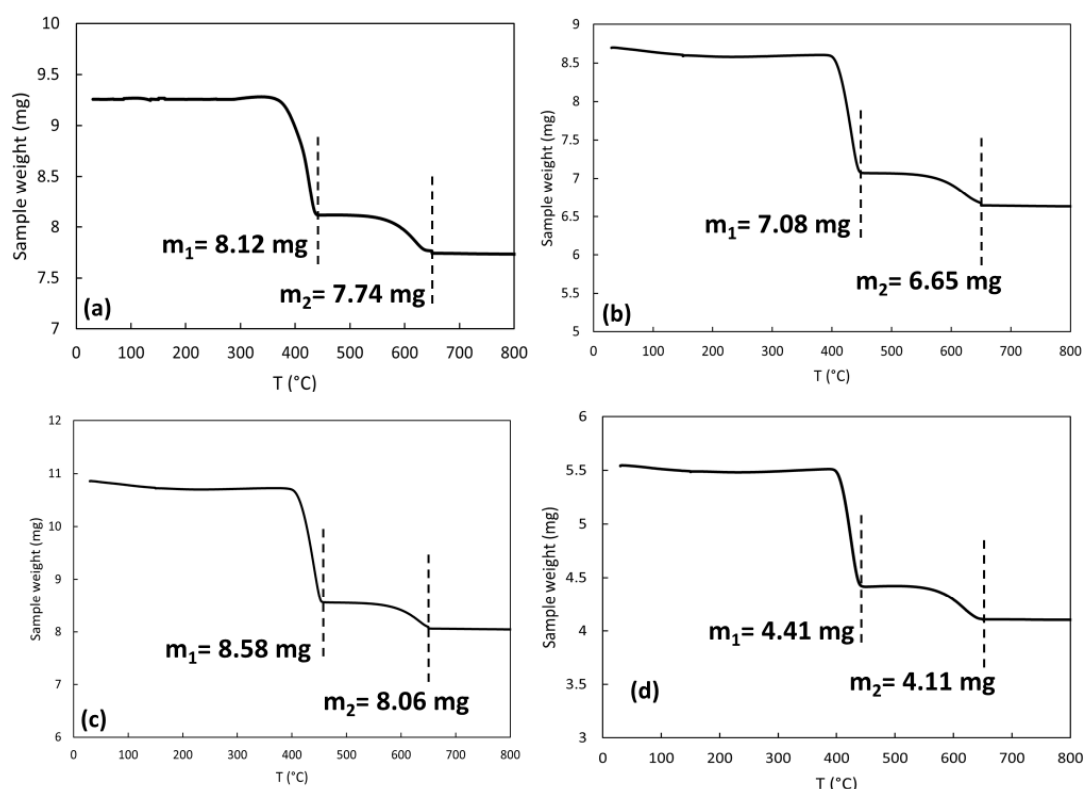


Figure 3-11 TGA curves of the used sorbent from the SESMR tests using (a) Ni/Al₂O₃, (b) Ni₃Cu₁/Al₂O₃, (c) Ni₃Fe₁/Al₂O₃, and (d) Ni₃Ge₁/Al₂O₃ as catalysts.

3.3.4 Microkinetic modelling of SMR and DFT calculations for the bimetallic systems

As mentioned in section 3.1, Ni₃Fe₁ was predicted to be one of the catalysts with the highest SMR activity. However, this is in contradiction to the results presented in this paper. In order to ascertain the cause of this difference between numerical and experimental results, and to further investigate the promoting effect of Cu and Ge in the bimetallic systems, a combined DFT and MKM study was conducted.

In the work by Xu et al. [5], DFT-calculated adsorption energies of carbon and oxygen on the (211) bimetallic surface were used to evaluate the catalytic activity of the materials, which are summarised in Table 3-5. However, based on results from the XRD analysis (section 3.3.1.5) and extensive literature data [43–46], only the (111), (200) and (220) phases are present in the reduced catalysts,

among which (111) is the most dominant. The catalytic activity of the bimetallic catalysts involved in this study is therefore mainly determined by the atomic/molecular adsorption energies of the species involved in the SMR reaction on the (111) surface. It is therefore possible that the difference between the prediction and the experimental results is due to a difference in surface energetics. To confirm this, we have calculated the adsorption energies of carbon and oxygen on the Ni(111), Ni₃Cu₁(111), Ni₃Fe₁(111), and Ni₃Ge₁(111) surfaces as these values are not all readily available from pre-existing literature. As can be seen from Table 3-5, there is a 0.1 – 0.8 eV difference between the adsorption energies on the (111) and (211) surfaces. The (211) surface shows a stronger adsorptive ability towards carbon in general, whereas its oxygen adsorptive ability is weaker in the case of Ni₃Fe₁ and Ni₃Ge₁.

To evaluate how different adsorption energies affect the overall catalytic activity for the SMR reaction, the eight materials listed in Table 3-5 were plotted against a “volcano plot” (Figure 3-12). The volcano plot was obtained from the microkinetic model developed using the approach described in the methodology section. The result shows the turnover frequency (TOF) of H₂ production as a function of the carbon and oxygen adsorption energies, which is a measurement of the material’s catalytic activity for the SMR reaction.

The four (211) surfaces are indicated by the triangles on the volcano plot. Ni(211), Ni₃Fe₁(211), and Ni₃Ge₁(211) are located in the central region of the plot, indicating the highest TOF (10^{-3} s^{-1}), and therefore highest catalytic activity. This is consistent with the previous prediction that Ni₃Fe₁ and Ni₃Ge₁ are the most active bimetallic catalysts for SMR. However, if the prediction is to be made based on the (111) surfaces (indicated by the crosses on the volcano plot), it is evidenced that Ni₃Cu₁ is the most optimal with a TOF of 10^{-4} s^{-1} . Ni₃Ge₁ was also shown to be an active catalyst with the second highest H₂ TOF. On the other hand, compared with Ni₃Fe₁(211), its (111) surface has a significantly lower carbon and oxygen adsorption energies, leading to a relatively lower catalytic activity. Based on the (111) surfaces, the relative activity of the mono and bimetallic catalysts was found to be Ni $\approx$ Ni₃Cu₁ > Ni₃Ge₁ > Ni₃Fe₁, which is consistent with the results obtained from the experimental testing. It can therefore

be concluded that the low catalytic activity of $\text{Ni}_3\text{Fe}_1/\text{Al}_2\text{O}_3$ is due to a combination of different factors – including both physical (surface segregation of Fe) and chemical properties (highly adsorptive to carbon and oxygen, low reducibility). This also indicates that the crystallite phase of a given catalyst can significantly influence its catalytic activity. The results are therefore also dependent upon the synthesis method employed during the experiments, and the amount of (111) surface produced in the synthesized samples.

It is also generally acknowledged that the method used for the DFT calculations (e.g., functionals, pseudopotentials, etc) can affect the final results obtained. It is therefore of interest that a systematic database be built for molecular and atomic adsorption on the (111) phase of transition metals and alloys, as it is usually the most exposed and close-packed surface in transition metal-based species. This will greatly facilitate the accurate prediction of catalytic activity for SMR and other reactions alike.

Table 3-5 Adsorption energies on the (111) surface (obtained by DFT calculations) and on the (211) surface (extracted from literature [5,44]).

Surface	Carbon adsorption energy (eV)	Oxygen adsorption energy (eV)	Surface	Carbon adsorption energy (eV)	Oxygen adsorption energy (eV)
Ni(111)	-7.9	-5.4	Ni(211)	-8.2	-5.5
$\text{Ni}_3\text{Cu}_1(111)$	-7.8	-5.3	$\text{Ni}_3\text{Cu}_1(211)$	-8.6	-5.6
$\text{Ni}_3\text{Fe}_1(111)$	-8.9	-6.4	$\text{Ni}_3\text{Fe}_1(211)$	-8.3	-5.7
$\text{Ni}_3\text{Ge}_1(111)$	-7.3	-5.9	$\text{Ni}_3\text{Ge}_1(211)$	-8.4	-5.5

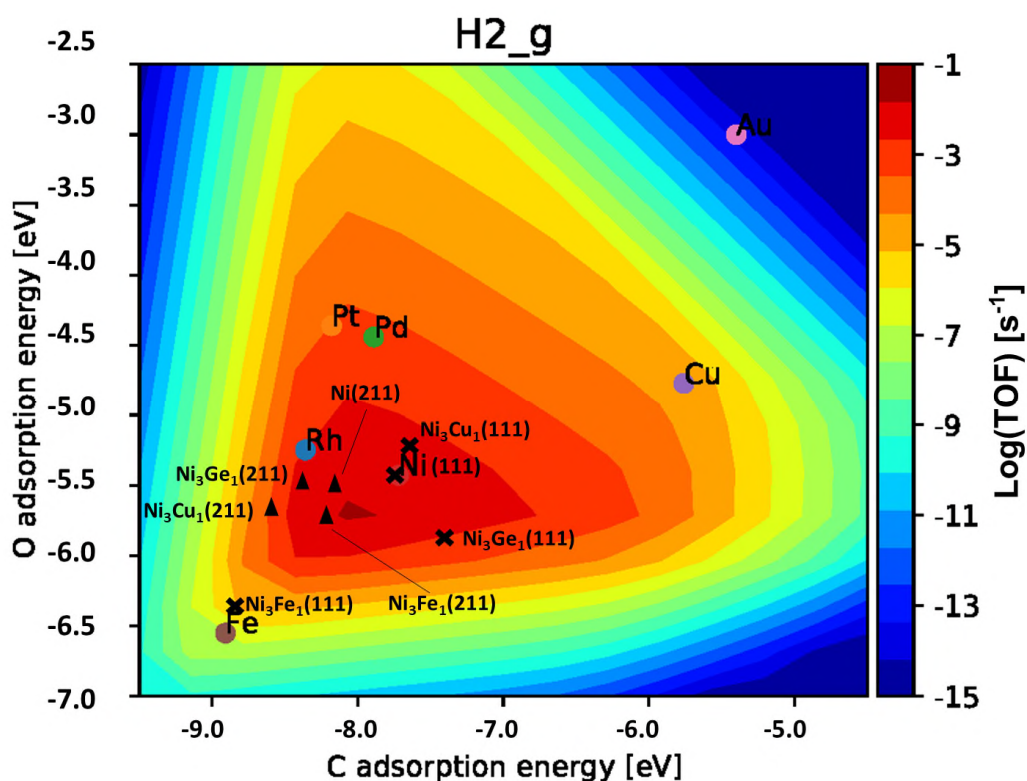


Figure 3-12 TOF of H₂ production as a function of carbon and oxygen adsorption energies.

3.4 Conclusions

Three bimetallic catalysts have been successfully synthesized using the wet impregnation method, and the formation of Ni-Cu, Ni-Fe, and Ni-Ge bimetallic solid solutions upon reduction was confirmed by XRD analysis. XRF and EDX analysis showed that Ni, Cu, and Ge were homogeneously distributed within the porous alumina support, whereas Fe tends to segregate on the outer layer of the support. The addition of Cu improved the overall surface area and metal dispersion rate compared to the monometallic Ni catalyst, whereas a slight decrease was observed for Fe and Ge. The optimal physical and chemical properties of the Ni₃Cu₁/Al₂O₃ catalyst were also reflected on its catalytic performance. The highest methane conversion of 87% for SMR tests was achieved by Ni₃Cu₁/Al₂O₃ at 800 °C under high GHSV condition, proving it to be a promising alternative to conventional Ni catalysts and noble metal-based catalysts. Similarly, the addition of Ge improved the overall activity of the

monometallic Ni catalyst, and the effect is most significant at high temperatures. The bimetallic Ni-Fe catalyst on the other hand, showed a lower activity compared to Ni. The experimental observations were also supported by ab-initio DFT calculations and microkinetic modelling. DFT calculations of molecular and atomic adsorption energies were carried out for the (111) and (211) surfaces of the mono and bimetallic materials, and a clear difference in their carbon and oxygen adsorption abilities was observed. This explained the inconsistency between the experimental results and the conclusions made based on previous numerical screening processes. The microkinetic model indicated that both $\text{Ni}_3\text{Ge}_1(111)$ and $\text{Ni}_3\text{Cu}_1(111)$ were able to achieve a similar level of hydrogen production rate as $\text{Ni}(111)$, whereas the $\text{Ni}_3\text{Fe}_1(111)$ surface is not suitable for the SMR reaction. TGA tests of the used catalysts showed that the carbon resistant ability of the catalysts was enhanced by the formation bimetallic alloys. However, further study is needed to investigate the stability of the materials under long-term SMR conditions. The addition of calcium oxide as the CO_2 sorbent enhanced the overall performance of all materials, with $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ reaching a methane conversion of 97% at 700 °C, which is close to the thermodynamic equilibrium level. Hydrogen yield and hydrogen purity were also improved by 30% and 20% respectively, proving SESMR to be a promising technology for low carbon hydrogen production. In conclusion, this combined experimental and numerical investigation of bimetallic catalysts has identified promising novel materials for the application of (SE)SMR and provided directions for future research in this field.

3.5 References

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4 Bimetallic Ni-Cu/Al₂O₃ catalysts for (sorption-enhanced) steam methane reforming

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Abstract

The catalytic performance of a monometallic Ni/Al₂O₃ and three bimetallic Ni-Cu catalysts (with Cu loading of 2.5, 5, and 7.5 mol%, respectively) for the (sorption-enhanced) steam methane reforming reaction was evaluated. Physico-chemical characterization of the materials confirmed the formation of Ni-Cu alloy and the even distribution of active metals within the porous high-surface area support. All three bimetallic catalysts showed enhanced methane conversion compared to the conventional Ni/Al₂O₃ catalyst at higher temperatures, which was attributed to the promotion of the water-gas shift reaction by the addition of Cu. The experimental observations were supported by the Density Functional Theory calculations of carbon and oxygen adsorption on the mono and bimetallic surfaces. Ni₃Cu₁ and Ni₁Cu₁ were calculated to have a similar level of catalytic activity as Ni, based on results from a microkinetic model of the steam methane reforming reaction. Ni₁Cu₃ showed slightly lower activity, potentially due to its low carbon adsorption ability which impedes the rate-determining methane decomposition process. The SMR reaction was further improved by adding calcium oxide as the CO₂ sorbent, which increased both methane conversion and hydrogen yield. Ni₃Cu₁/Al₂O₃ and Ni₁Cu₁/Al₂O₃ were identified as promising SMR catalysts with a high methane conversion of approximately 90% at 800 °C and 97% at 700 °C, without and with the sorbent, respectively.

Keywords:

Bimetallic Ni-Cu catalyst; Steam methane reforming; Sorption-enhanced steam methane reforming; Hydrogen production; Density Functional Theory; Microkinetic modelling

4.1 Introduction

Steam methane reforming (SMR) is currently the primary route for catalytic hydrogen production which accounts for over 50% of the world's hydrogen production [1]. In the SMR process, steam and methane react under high temperatures and pressures and in the presence of a catalyst to produce a mixture of carbon monoxide, carbon dioxide, and hydrogen [2]. Most industrial SMR catalysts are based on using nickel as the active component, however, the use of bimetallic catalysts has gained increasing attention over the past years due to their enhanced performance [3,4]. Although Ni-based catalysts promoted by platinum group metals have been shown to have optimal performance, in terms of both catalytic activity [5] and resistance to coke and sulphur [6], industrial application of these materials can be limited by their high cost. Bimetallic Ni-Cu catalysts emerged as a promising alternative for the reforming of small hydrocarbons due to their high availability, good catalytic activity and stability. Ni-Cu catalysts have been extensively studied for dry methane reforming [7]. The addition of Cu was found to enhance the overall activity while promoting the reducibility and sintering resistance of the alloy nanoparticles. Khzouz et al. carried out a series of tests to evaluate the performance of Ni-Cu catalysts for methanol reforming [8] and low-temperature SMR [9,10]. They concluded that compared with the conventional commercial Ni/Al₂O₃ catalyst, the bimetallic materials showed a similar level of catalytic activity with less coke formation. The highest Cu loading that can be achieved without negatively affecting its activity was found to be 5 wt.%.

Apart from optimizing the catalysts, the overall SMR process can also be further improved. One promising novel technology – sorption-enhanced steam methane reforming (SESMR) – allows for the production of high-purity hydrogen with simultaneous *in-situ* carbon capture using a CO₂ sorbent (e.g. CaO). The

equations of all reactions taking place in both SMR and SESMR can be found in section 2.1.

Although SESMR is considered a promising technology for low-carbon high-purity hydrogen production, some key challenges remain to be solved, including the development of cost-effective and stable catalysts to improve conversion efficiency [11]. In our previous work [12], a preliminary study was carried out to investigate the effect of adding a low concentration of Cu (2.5 wt.%) to Ni/Al₂O₃ catalyst. The bimetallic catalyst showed enhanced activity for SMR, especially at higher temperatures. In this work, a series of bimetallic Ni-Cu/Al₂O₃ catalysts (with Cu loading of 2.5, 5, and 7.5 wt.%) were tested under both SMR and SESMR conditions to understand the effect of Cu loading on the overall performance of the catalysts. The experimental results were further confirmed and explained by Density Functional Theory (DFT) calculations of the carbon and oxygen adsorption abilities of the catalysts, combined with results from a Microkinetic Model (MKM) of the SMR reaction.

4.2 Experimental

4.2.1 Catalyst preparation

A monometallic Ni/Al₂O₃ catalyst and three supported bimetallic Ni-Cu/Al₂O₃ catalysts (with Ni:Cu molar ratios of 3:1, 1:1, and 1:3, respectively) were synthesized by impregnating the alumina support (gamma-phase, bimodal, Alfa Aesar) with the aqueous solution of nickel nitrate (Ni(NO₃)₂·6H₂O, 99%, Fisher Scientific), and copper nitrate (Cu(NO₃)₂·2.5H₂O, 98%, Fisher Scientific). An appropriate amount of metal precursors was dissolved in deionised water so that the total metal loading in the reduced samples is equal to 10 wt.%. The impregnated alumina support was agitated in an ultrasonic tank for 3 hours. The samples were then dried in a static oven overnight, followed by calcination at 600 °C for 4 h with a heating rate of 5 °C/min. Finally, the samples were reduced with 10% H₂ in N₂ at 600 °C for 20 min.

4.2.2 Characterization

The X-ray fluorescence spectroscopy (XRF) was carried out using a micro-XRF Bruker M6 Jetstream. Data was acquired at 30 kV and 600 μ A, with quantification calculated using the “Fundamental Parameters” approach.

The scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were carried out using a TESCAN VEGA 3 scanning electron microscope.

N₂ adsorption and desorption isotherms were obtained using a Micromeritics 3Flex. Prior to the physisorption tests, the samples were degassed at 400 °C for 5 h with a heating rate of 10 °C/min to remove any moisture or impurities. The surface area of the samples was calculated using the Brunauer–Emmett–Teller (BET) equation, and the total pore volume and median pore diameter were obtained from the Barrett-Joyner-Halenda (BJH) method. Tests for each sample were repeated three times to ensure the repeatability of the data, the average values were calculated and presented in this paper.

The Micromeritics 3Flex was also used for the pulse H₂ chemisorption tests. Approximately 1 g of sample was reduced at 600 °C for 30 min by pure hydrogen, followed by degassing and cooling in an N₂ stream. A hydrogen stream was then pulsed over the sample 10 times or until the area of the peaks was stable, indicating no further adsorption of H₂ by the sample. Similarly, three tests were conducted for each sample and the average was calculated.

The X-ray diffraction (XRD) analysis was carried out using the Siemens D5005 X-ray Diffractometer with Cu K α radiation. The reduced samples were crushed into a powder and scanned in the 2 θ range of 30° – 80° with a step size of 0.02°.

The X-ray Photoelectron Spectroscopy (XPS) analysis was carried out using a Thermofisher ESCALAB 250 electron spectrometer. An Al K α X-ray source with a single energy level was employed to optimise resolution. The experiments maintained a source excitation energy of 15 KeV, an emission current of 6 mA, an analyser pass energy of 20 eV, a step size of 0.1 eV, and a dwell time of 50 ms. Throughout the examinations, the spectrometer consistently maintained a base pressure better than 5×10^{-10} mbar, ensuring that all recorded signals originated from the sample surface.

Thermogravimetric analysis (TGA) of the used catalysts was carried out using a Perkin Elmer TGA 8000. Prior to the TGA tests, all samples were reduced by hydrogen and degassed at 400 °C for 24 h to ensure no metal oxides or impurities were present. Approximately 20 mg of the sample was oxidized in air while being heated from 30 to 1000 °C with a heating rate of 10 °C/min. The change in sample weight during the oxidation process is equal to the difference between the weight loss due to carbon combustion, and the weight increase due to metal oxidation. The degree of carbon formation is evaluated using the following equation:

$$\text{carbon amount (wt. \%)} = \frac{\text{weight of carbon deposited on the sample}}{\text{weight of sample used for TGA}}$$

4.2.3 Evaluation of catalytic activity

The same fixed bed reactor mentioned in section 3.2.3 and described in the work by Shen et al. [13] was used to test the catalytic activity of the catalysts. All tests were carried out under atmospheric pressure, using 10 vol.% methane in nitrogen, with a steam to carbon ratio of 3 and a gas hourly space velocity (GHSV) of 15,000 h⁻¹. The SMR tests were carried out at 600, 700, and 800 °C with approximately 2.5 g of catalyst. The catalysts were reduced in 10 vol.% hydrogen in nitrogen at 600 °C prior to the SMR tests. The SESMR tests were carried out at 600, 650, and 700 °C using approximately 2.5 g of catalyst mixed with 3 g of limestone (Longcliffe). The materials were activated in 10 vol.% hydrogen in nitrogen at 850 °C for the reduction of the active metals and the calcination of the sorbent.

The performance of the catalysts was evaluated based on four parameters – CH₄ conversion, H₂ yield, H₂ purity (dry and N₂ free-based), and CO selectivity. The equations used for calculating these parameters were detailed in section 3.2.3.

4.2.4 Density Functional Theory

The DFT calculations of the carbon and oxygen adsorption energies on the close-packed Ni(111), Ni₃Cu₁(111), Ni₁Cu₁(111) and Ni₁Cu₃(111) surfaces were performed using the open-source software package Quantum Espresso [14]. The ionic cores were described by the projector augmented wave (PAW) method [15].

The generalized gradient approximation (GGA) functional with the Perdew-Burke-Ernzerhoff (PBE) functional was used to describe the exchange-correlation [16]. The spin polarization effect was considered in all calculations as nickel is a magnetic element. The wave functions at each k-point are expanded with a plane-wave basis set with a kinetic energy cut-off of 25 Rydberg. The metallic surfaces were simulated with (2×2) supercell separated by a 10 Å vacuum on the Z direction. Each slab contains four layers of atoms with the bottom two layers fixed, and the top two relaxed. The adsorption energy was calculated as:

$$E_{ads} = E_{adsorbate+slab} - E_{adsorbate} - E_{slab}$$

Where $E_{adsorbate+slab}$, $E_{adsorbate}$ and E_{slab} are the total energies of the surface with the adsorbed molecule, the molecule in the gas phase and the clean slab, respectively. Brillouin zone sampling of the surface slabs was performed using a $3 \times 3 \times 1$ grid.

For the monometallic Ni(111) surface, four high-symmetry adsorption sites were considered – top, bridge, FCC (three-fold site with no atom on the layer below), and HCP (three-fold site with an atom on the layer below). For the bimetallic surfaces, eight different high-symmetry adsorption sites were considered and the locations and detailed definitions of each site are illustrated in Figure 4-1. The adsorption energies of a given adsorbate on each of the adsorption sites were compared, and the lowest one was selected as the final adsorption energy as it represents the most stable structure.

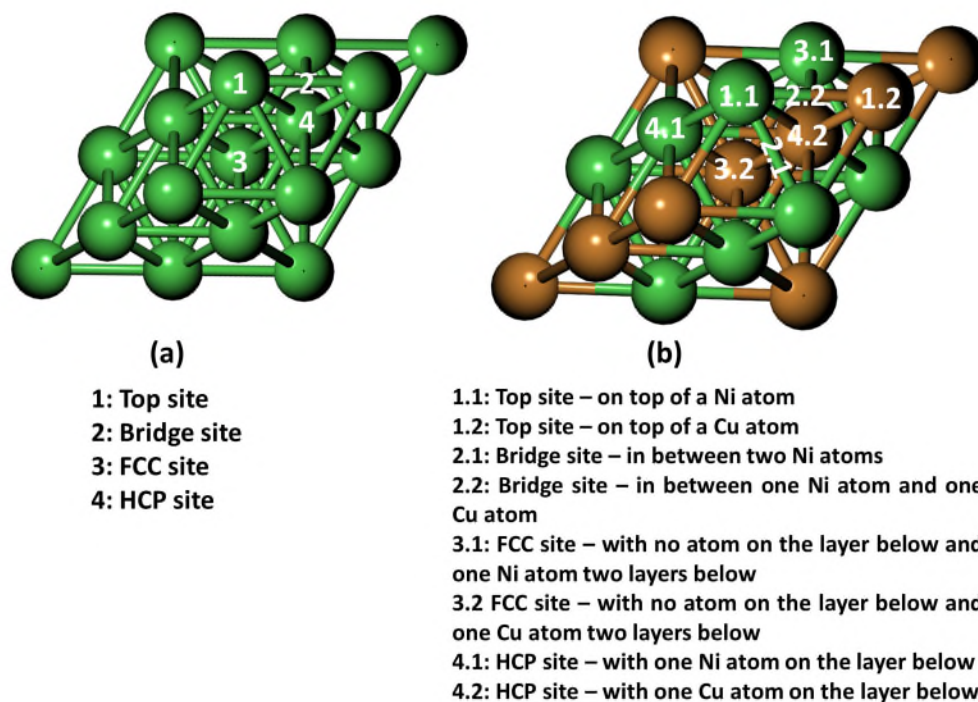


Figure 4-1 Illustration of the adsorption sites on the (a) monometallic surfaces and (b) bimetallic surfaces. (Green atoms: Ni, brown atoms: Cu.)

4.2.5 Microkinetic modelling

The microkinetic model of the SMR reaction was developed using the CatMAP Python module [17]. The model was built based on the atomic and molecular adsorption on 7 common transition metal surfaces, including Ni, Cu, Fe, Rh, Pt, Pd, and Au. The elementary reaction steps considered in the model are summarized in Figure 4-2. Details of the input parameters and the numerical values of the energetics involved in the model can be found in our previous work [12].

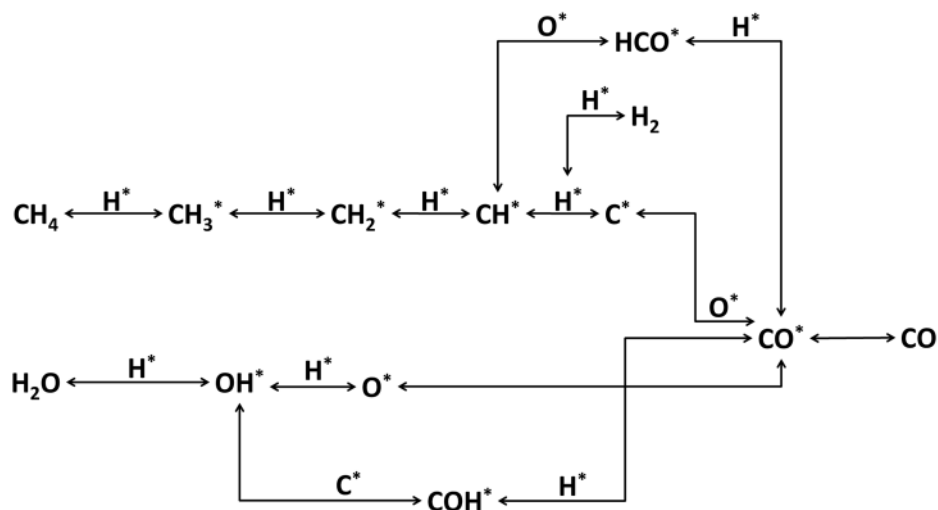


Figure 4-2 Reaction pathway of the SMR reaction.

4.3 Results and discussion

4.3.1 Characterization

4.3.1.1 XRF analysis

Results from the XRF analysis are summarized in Table 4-1. Although the total metal loading of $\text{Ni}/\text{Al}_2\text{O}_3$, $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$, and $\text{Ni}_1\text{Cu}_3/\text{Al}_2\text{O}_3$ are slightly lower than the theoretical value of 10 wt.%, the differences between the theoretical and measured values are all within 6%. Similarly, the measured Ni:Cu ratios are very close to the theoretical values with negligible errors. The composition of the samples is therefore considered to be accurate.

Table 4-1 Theoretical and measured total metal loading and Ni:Cu molar ratio.

	Total metal loading (wt.%)		Ni:Cu molar ratio	
	Theoretical	Measured	Theoretical	Measured
$\text{Ni}/\text{Al}_2\text{O}_3$	10	9.5	-	-
$\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$		10.0	3 : 1	2.8 : 1.0

Ni ₁ Cu ₁ /Al ₂ O ₃	9.8	1 : 1	1.0 : 1.0
Ni ₁ Cu ₃ /Al ₂ O ₃	9.4	: 3	1.0 : 2.9

4.3.1.2 SEM-EDX analysis

Prior to the SEM-EDX analysis, the cylindrical catalyst pellets were cut in half, and the SEM images of the inner section of the synthesized materials are presented in Figure 4-3. As there is no visible difference between the morphology of the three bimetallic catalysts, only the images of Ni₁Cu₁/Al₂O₃ are presented in this paper. Figure 4-3 (a) and (b) show the morphology of the outer layer of the catalyst pellets. The calcined pellets have a relatively smooth surface, with both large openings and smaller pores (circled in red) to provide access to the inner structure of the porous alumina support. A further zoom into the inner sections of the catalysts provides the morphology of the deposited metal particles, shown in Figure 4-3 (c) and (d). The particles are estimated to be in the range of 5 – 20 μm and are evenly distributed within the support. Distribution of the elements within the inner section of the calcined catalysts was obtained by EDX analysis and the elemental mappings are presented in Figure 4-4. It can be observed that the composition of the active metals is similar to the bulk material, indicating that both metal precursors were able to penetrate the support effectively during the impregnation process. Both Ni and Cu are evenly distributed within the samples and no apparent phase segregation or agglomeration was observed. The morphology of the catalysts is considered to be ideal for the SMR process – the highly porous structure of the support ensures the efficient gas diffusion process and the uniform distribution of Ni and Cu within the support provides the active sites for reactions to take place.

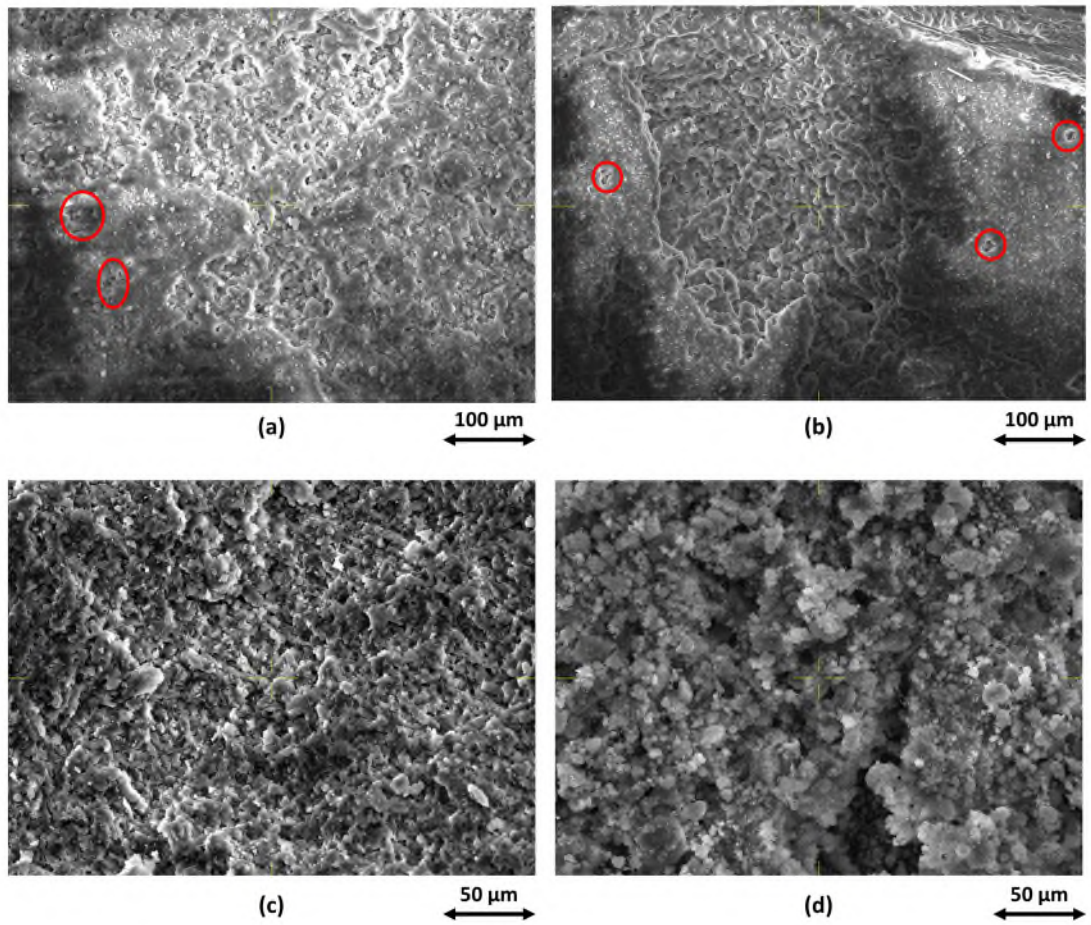


Figure 4-3 SEM images of the outer layer of the (a) Ni/Al₂O₃ and (b) Ni₁Cu₁/Al₂O₃ pellets, and the particles of (c) Ni/Al₂O₃ and (d) Ni₁Cu₁/Al₂O₃.

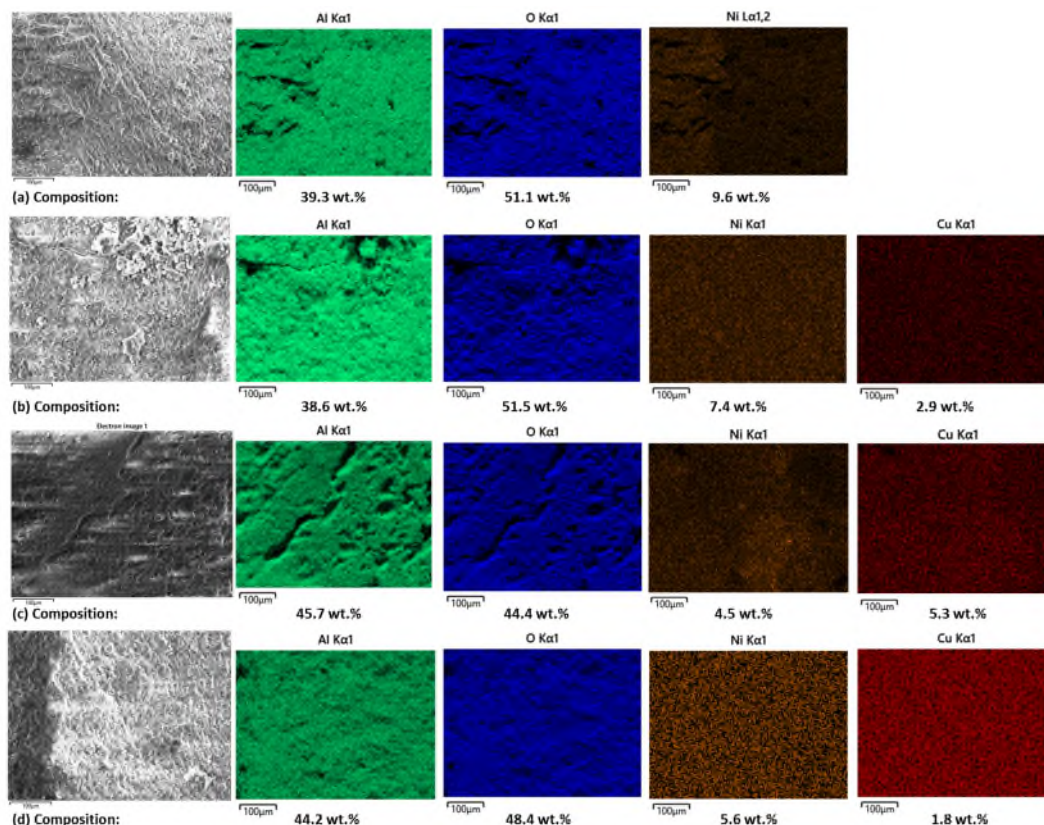


Figure 4-4 EDX elemental mapping of (a) Ni/Al₂O₃, (b) Ni₃Cu₁/Al₂O₃, (c) Ni₁Cu₁/Al₂O₃, (d) Ni₁Cu₃/Al₂O₃.

4.3.1.3 Physisorption

The results obtained from the N₂ physisorption analysis are summarised in Table 4-2, the isotherms obtained from the tests are available in Supplementary Information. The isotherms are consistent with type IV mesoporous materials with the type H₃ hysteresis loop, indicating the potential formation of parallel plate-shaped pores [18]. All samples showed a mono-modal distribution of pore size, with a median diameter of ~ 12 nm. The untreated alumina support has a BET surface area of 227.2 m²/g, pore volume of 0.77 cm³/g, and median pore diameter of 12.22 nm. The high surface area and porous structure of the support contributed to the facile dispersion of active metals. Compared to the bare support, all metal-loaded samples exhibited smaller surface area and pore volume, as nickel and copper particles may block the pores of alumina during the impregnation process [19,20]. The surface area, pore volume and pore size then slightly increased after the reduction process due to the removal of metal oxide

species with hydrogen. The pore diameter of approximately 12.5 nm of all samples is able to decrease the diffusion resistance within the support [21], contributing to the reaction between gaseous species on the active metal surface. The small pore size of Ni/Al₂O₃-based catalysts is also beneficial for decreasing the sintering rate during the SMR reaction [22].

Table 4-2 Results from N₂ physisorption analysis.

	BET surface area (m ² /g)		BJH adsorption pore volume (cm ³ /g)		BJH adsorption median pore diameter (nm)	
Alumina	227.2		0.77		12.22	
	Fresh	Reduced	Fresh	Reduced	Fresh	Reduced
Ni/Al ₂ O ₃	190.3	227.7	0.62	0.77	11.96	12.37
Ni ₃ Cu ₁ /Al ₂ O ₃	217.0	222.4	0.69	0.77	11.50	12.56
Ni ₁ Cu ₁ /Al ₂ O ₃	180.1	200.9	0.66	0.76	11.44	12.39
Ni ₁ Cu ₃ /Al ₂ O ₃	226.2	228.6	0.77	0.78	12.35	12.42

4.3.1.4 Chemisorption

The hydrogen uptake amount, metal dispersion rate, metallic surface area, and crystallite size of the catalysts obtained by pulse H₂ chemisorption analysis are summarized in

Table 4-3. The highest H₂ uptake amount of 14.04 μmol/g was achieved by Ni/Al₂O₃, with a metal dispersion of 1.07%. A gradual decrease in H₂ uptake amount, metal dispersion, and metallic surface area was observed as Cu loading in the samples increased. This is as expected as the concentration of surface Ni atoms was diluted by the increasing amount of Cu atoms, which are less active in H₂ adsorption compared to Ni [23]. It is also observed that a Cu concentration of 7.5 at.% significantly increased the crystallite size to ~ 3,000 Å, which may lead to pore blocking within the support.

Table 4-3 Results from H₂ pulse chemisorption analysis.

	H ₂ uptake ($\mu\text{mol/g}$)	Metal dispersion (%)	Metallic surface area		Crystallite size ($\text{\AA}$)
			m^2/g sample	m^2/g metal	
Ni/Al ₂ O ₃	14.04	1.07	0.56	5.56	1,092
Ni ₃ Cu ₁ /Al ₂ O ₃	9.43	1.56	0.37	5.33	757
Ni ₁ Cu ₁ /Al ₂ O ₃	8.28	0.72	0.37	3.71	1,218
Ni ₁ Cu ₃ /Al ₂ O ₃	2.76	0.22	0.11	1.12	3,005

4.3.1.5 XRD analysis

The XRD patterns of the bare alumina support and the reduced bimetallic catalysts are presented in Figure 4-5. The alumina support was shown to be amorphous, as no crystallite peak was detected. The three sets of peaks in the range of 43° – 44°, 50° – 52°, and 74° – 76° observed in Figure 4-5 (a) correspond to the (111), (200), and (220) phases of the Ni-Cu alloy. The formation of bimetallic Ni-Cu alloy in the samples was confirmed by comparing the diffraction peaks with that of pure Ni and Cu [24], as shown in Figure 4-5 (b). The diffraction peaks of the bimetallic catalysts shift towards lower intensities as Cu loading increases, indicating an increase in the lattice size of the Cu-rich samples. The slight splitting in the diffraction peaks of the Ni₁Cu₃/Al₂O₃ sample is potentially due to the formation of a small amount of segregated copper-rich phases due to the high Cu loading [25].

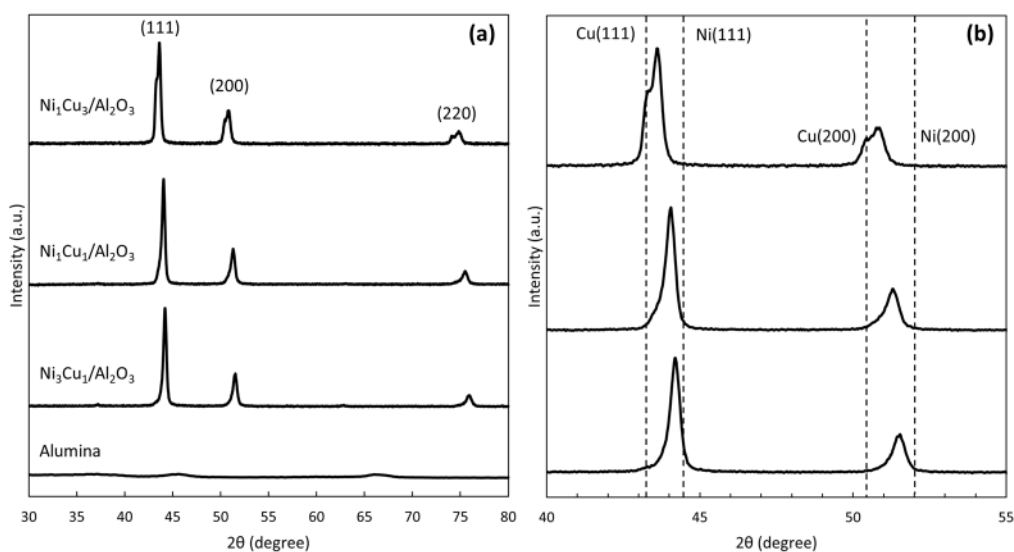


Figure 4-5 XRD patterns of the alumina support and bimetallic Ni-Cu catalysts:
(a) overall pattern, (b) zoomed-in image of the 2θ range of $40^\circ - 55^\circ$.

4.3.1.6 XPS analysis

The XPS profiles of the reduced monometallic Ni/Al₂O₃ and bimetallic Ni-Cu catalysts are presented in Figure 4-6. Two main peaks centred at approximately 856.2 and 873.5 eV are observed in the Ni 2p spectra (Figure 4-6 (a)), which correspond to the 2p 3/2 and 2p 1/2 peak of Ni²⁺ (NiO) with strong interaction with the alumina support [26,27]. Two satellite peaks with lower intensity were observed at the higher binding energy side of the main peaks, which is a typical characteristic of NiO [28]. An additional peak at approximately 853 eV was observed for Ni/Al₂O₃, corresponding to the metallic Ni⁰. In the Cu 2p spectra (Figure 4-6 (b)), the two main peaks centred at approximately 934 and 953.5 eV are assigned to Cu²⁺ 2p 3/2 (CuO) and a combination of Cu²⁺ 2p 1/2 (CuO) and Cu⁰ 2p 1/2, respectively. It is also observed that the peaks at 934 eV shift to a higher binding energy as the concentration of Ni increases, which is attributed to the electron transfer from Cu to Ni due to the formation of Ni-Cu alloy [26]. The presence of metal oxide species in the reduced samples is possibly due to the inevitable reoxidation of the samples during storage, transportation, and the XPS analysis process.

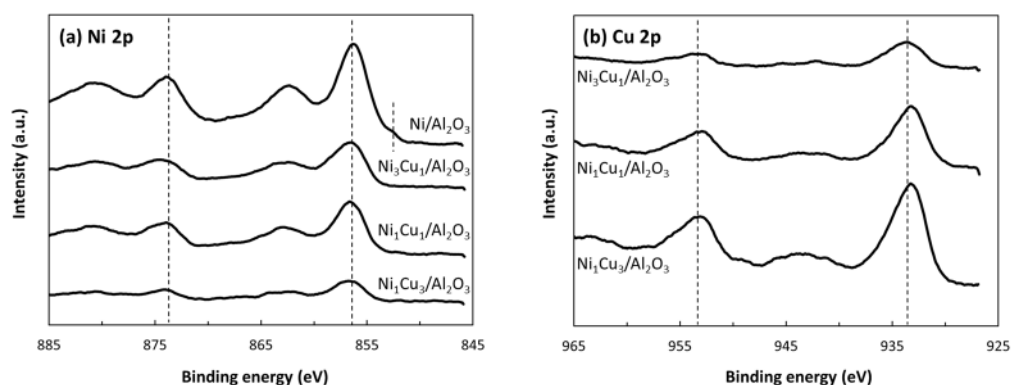


Figure 4-6 XPS profiles of the monometallic Ni/Al₂O₃ and bimetallic Ni-Cu catalysts: (a) Ni 2p spectra, (b) Cu 2p spectra.

4.3.2 Catalytic performance study for steam methane reforming

The catalytic performance of the catalysts was evaluated based on CH₄ conversion, H₂ yield and purity, and CO selectivity. Tests using Ni₃Cu₁/Al₂O₃ as the catalyst were repeated three times for each temperature to ensure the repeatability of the experiments, and the standard deviation error bars were plotted against the results shown in Figure 4-7.

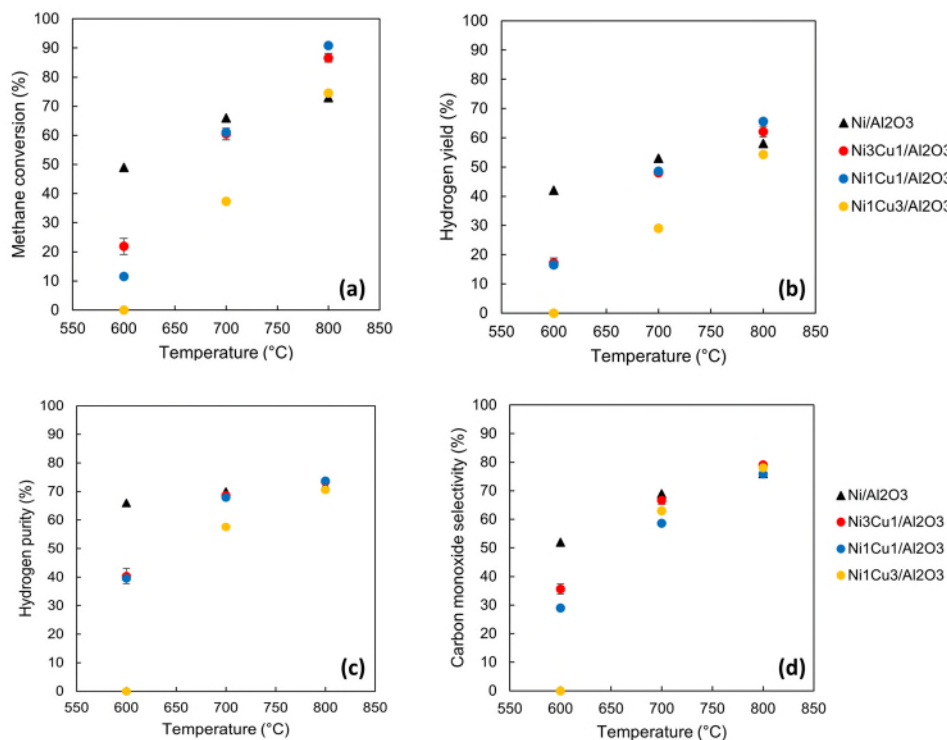


Figure 4-7 (a) Methane conversion, (b) hydrogen yield, (c) hydrogen purity, and (d) CO selectivity of Ni/Al₂O₃ and the bimetallic Ni-Cu catalysts under SMR conditions.

Due to the endothermic nature of the SMR reaction, CH₄ conversion for all catalysts showed an increase with the reaction temperature. Ni₁Cu₃/Al₂O₃ showed no catalytic activity at 600 °C. This is partly due to its relatively high Cu loading, as monometallic 10 wt.% Cu/Al₂O₃ was found to be inactive for SMR at lower temperatures [9]. The promoting effect of Cu becomes increasingly significant as temperature rises and all three bimetallic catalysts achieved a better performance at 800 °C compared to Ni/Al₂O₃. Both Ni₃Cu₁/Al₂O₃ and Ni₁Cu₁/Al₂O₃ reached a high CH₄ conversion level of 87% and 91%, respectively. Hydrogen yield and purity showed a similar trend as CH₄ conversion – Ni₃Cu₁/Al₂O₃ and Ni₁Cu₁/Al₂O₃ achieved a hydrogen yield of approximately 65% and 74% at 800 °C, higher than that of the monometallic Ni catalyst. CO selectivity is a parameter which measures the extent of the WGS reaction, a lower CO selectivity indicates that carbon is preferably converted to CO₂ in the system. Based on Figure 4-7 (d), all catalysts showed a similar level of CO selectivity at 800 °C. However, the CH₄ conversion of the bimetallic catalysts is shown to be

higher than Ni/Al₂O₃ (Figure 4-7 (a)), which indicates that carbon in the bimetallic systems was more likely to be converted to CO₂. It can therefore be concluded that the overall performance of the bimetallic Ni-Cu catalysts is enhanced by promoting the WGS reaction. The optimal Cu loading was found to be 5 wt.%, as Ni₁Cu₁/Al₂O₃ achieved the highest CH₄ conversion, H₂ yield, and H₂ purity. A lower Ni concentration is also desirable for potential large-scale application of the novel bimetallic catalyst, as copper is more cost-effective and less toxic in comparison to nickel.

During the experimental testing process, each catalyst was subjected to approximately 1.5 h of SMR reaction (with temperatures consecutively increasing from 600 to 800 °C). The used catalysts were characterized using N₂ physisorption and TGA, and the results are summarized in Table 4-4. Compared with the reduced catalysts, the used catalysts showed a smaller surface area and larger pore diameter with similar pore volume, which is potentially due to the sintering of the catalysts under high reaction temperatures. All catalysts showed very good coke resistance with less than 5 wt.% carbon deposition. Compared with the monometallic Ni catalyst, the addition of Cu decreased the amount of carbon formed and the effect was more significant for higher Cu loading. This is consistent with the observations reported by Khzouz et al. [10] and Djaidja et al. [29], where the addition of 2.5 – 5 wt.% Cu largely improved the coke resistance of the catalysts. The coke-resistant ability of the binary Ni-Cu system can be attributed to the formation of Ni-Cu alloy and the good dispersion of the two elements, which prevents the formation of bulk Ni particles susceptible to coke formation [29]. Ni-Cu alloy also has a weaker carbon binding ability compared to monometallic Ni, which is confirmed by the DFT-calculated adsorption energies presented in Table 4-5. This also prevented coke formation due to the methane decomposition process. It should be noted that the coke formation amount calculated in this work was only based on short-term SMR tests, it is recommended that a long-term test (e.g. > 20 h) be carried out to evaluate the effect of operation time on product yield and catalyst morphology.

Table 4-4 Characterization of the used catalysts after SMR tests.

	BET surface area (m ² /g)	BJH adsorption pore volume (cm ³ /g)	BJH adsorption median pore diameter (nm)	Carbon amount (wt.%)
Ni/Al ₂ O ₃	180.9	0.65	12.37	3.37
Ni ₃ Cu ₁ /Al ₂ O ₃	192.4	0.76	14.46	2.26
Ni ₁ Cu ₁ /Al ₂ O ₃	182.2	0.71	14.20	2.10
Ni ₁ Cu ₃ /Al ₂ O ₃	162.1	0.66	15.08	1.97

4.3.3 Catalytic performance study for sorption-enhanced steam methane reforming

As discussed in section 4.3.2, both Ni₃Cu₁/Al₂O₃ and Ni₁Cu₁/Al₂O₃ showed significant improvement in SMR activity compared with the conventional monometallic Ni catalyst. Further tests were therefore carried out to evaluate the performance of both materials under SESMR conditions. The SESMR tests were carried out at lower temperatures ($T = 600, 650, \text{ and } 700\text{ }^{\circ}\text{C}$) and the corresponding CH₄ conversion, H₂ yield, H₂ purity, and CO selectivity are presented in Figure 4-8.

The influence of reaction temperature on the SESMR process is a combined effect of temperature on the SMR reaction, the WGS reaction, and the adsorption of CO₂ absorption by CaO. As shown in Figure 4-8 (a) and (b), both CH₄ conversion and H₂ yield increased with temperature, indicating that the effect of endothermic SMR offsets the negative impact of the exothermic reactions in the temperature range of 600 – 700 °C. Both Ni/Al₂O₃ and Ni₃Cu₁/Al₂O₃ achieved very high CH₄ conversion of over 95% at 700 °C, which is approximately 25% higher than that without the presence of the sorbent. A further increase in temperature to improve the overall performance is considered unnecessary, as higher temperatures are unfavourable for CO₂ absorption and may accelerate the deactivation of the catalysts. SESMR is therefore a promising alternative to the conventional SMR, as a similar or better level of CH₄ conversion and H₂ yield can be achieved at lower temperatures. This reduces the energy consumption of the

system and is also beneficial for the long-term stability of the catalysts. On the other hand, unlike in the previous scenario where higher temperatures are favoured for H₂ purity and CO selectivity (Figure 4-7 (a) and (b)), both H₂ purity and CO selectivity slightly decreased as reaction temperature increased. This is due to the exothermic nature of the carbonation process – a CO₂ capture efficiency higher than 95% can only be achieved at temperatures lower than 600 °C [30].

The improvement in catalytic activity through the sorption of CO₂ is attributable to various factors, as the CO₂ produced by the WGS reaction interacts with the catalyst in different ways. CO₂ participates in the competitive adsorption of reactant gases on the catalyst surface [31,32]. By chemically adsorbing on the catalyst surface, CO₂ in the reaction system takes up more active adsorption sites and impedes the adsorption and reaction of CH₄ and H₂O molecules. By capturing the CO₂ using a solid sorbent, more available active adsorption sites can be released and utilized for the reaction between CH₄ and H₂O. Moreover, less CO₂ in the system favours the equilibrium of the WGS reaction towards the direction of more hydrogen production, thus improving the selectivity of the catalyst towards CO.

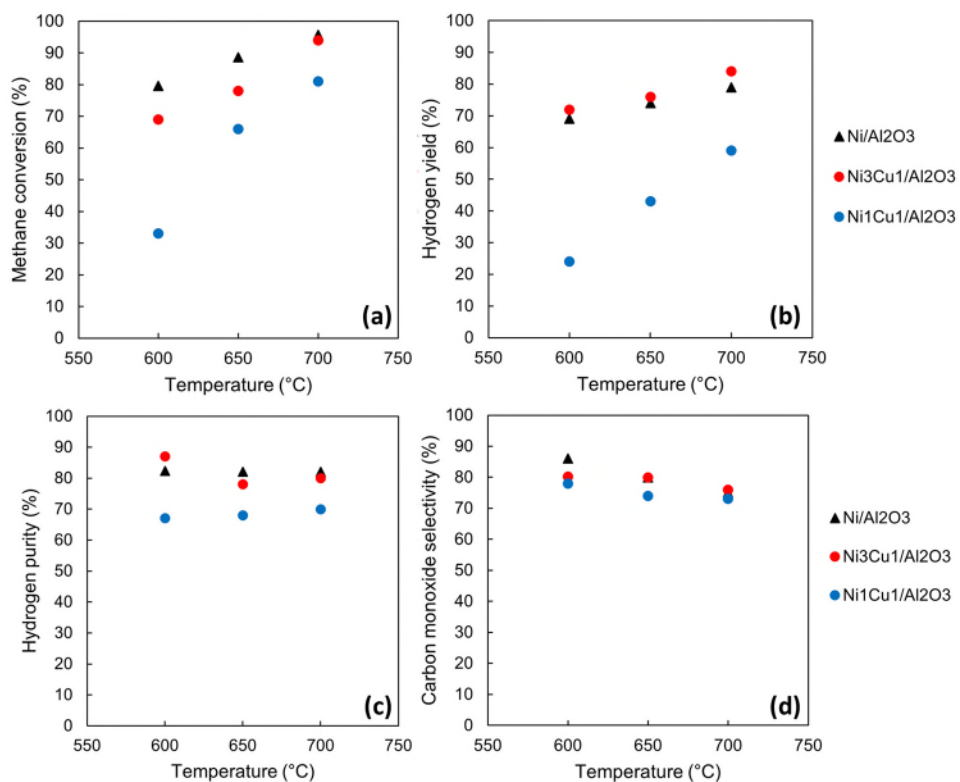


Figure 4-8 (a) Methane conversion, (b) hydrogen yield, (c) hydrogen purity, and (d) CO selectivity of Ni/Al₂O₃ and the bimetallic Ni-Cu catalysts under SESMR conditions.

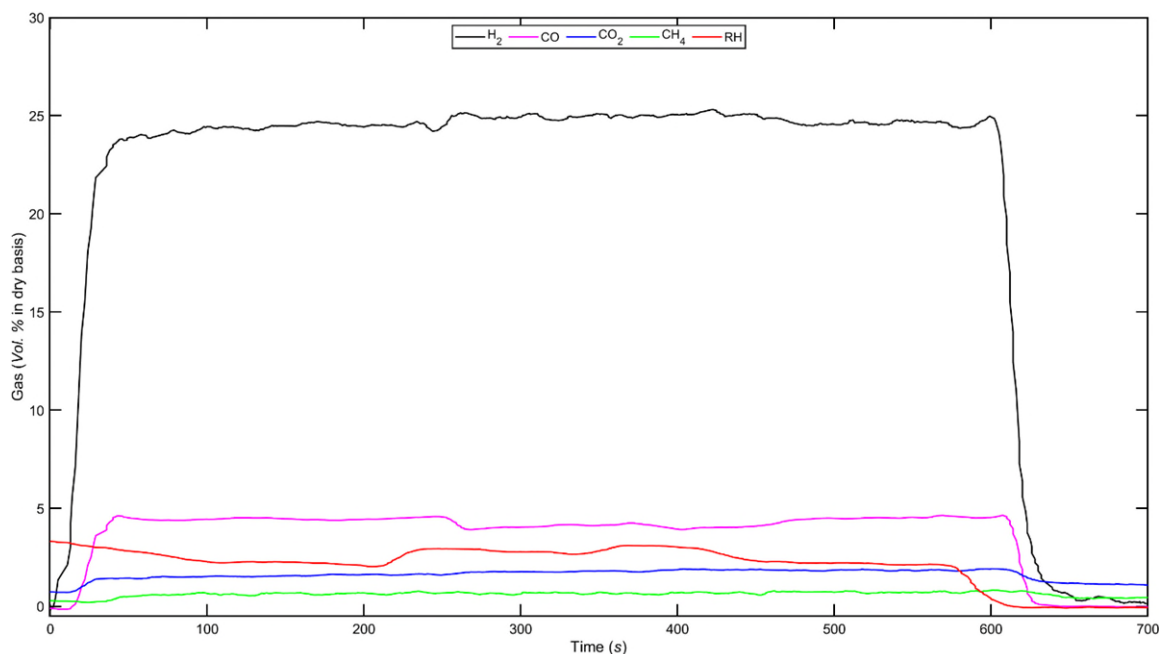


Figure 4-9 Composition of the outlet gas stream for SESMR at 700 °C (using Ni₃Cu₁/Al₂O₃ as the catalyst).

Figure 4-9 illustrates the composition of the outlet gas stream (balanced in N₂) during the pre-breakthrough period of the SESMR process, with a reaction temperature of 700 °C and using Ni₃Cu₁/Al₂O₃ as the catalyst. It can be observed that the partial pressure of CO₂ in the outlet stream is approximately 2%. However, with a stoichiometric or excess amount of CaO sorbent in the system, the equilibrium CO₂ partial pressure which can be reached during the pre-breakthrough period is equal to zero (all CO₂ produced by the WGS reaction is completely absorbed) [33,34]. This indicates that at this stage, the reaction is kinetically controlled rather than limited by equilibrium, as the equilibrium CO₂ pressure has not been reached. Concerning the kinetics aspect of the process, the carbonation reaction is generally considered to be kinetically controlled in a two-step manner [35]. At the very beginning, the reaction is kinetically controlled by the formation of CaCO₃ from CaO and CO₂. As the carbonation proceeds, the remaining CaO particles are covered by the freshly formed CaCO₃, limiting the diffusion of reactant gases. In this study, the sorbent and catalysts were introduced into the reactor after being physically mixed. It is therefore probable that the CaCO₃ formed during the pre-breakthrough period covered up the

sorbent and catalyst particles, thus limiting the kinetics of both the carbonation and the SMR reactions.

4.3.4 DFT calculations and microkinetic modelling

To further investigate how the concentration of Cu influences the catalytic activity of the bimetallic catalysts, DFT calculations of C and O adsorption on the monometallic Ni and Cu surfaces and the three bimetallic surfaces were carried out. In this work, we focused on the adsorption of C and O atoms only as they were proven to be the rate-determining factors for the SMR reaction [36,37]. The (111) surface was selected as it is the most close-packed surface for crystals with the face-centred cubic structure, and the most dominant surface in the catalysts synthesized in this study based on the XRD analysis (section 4.3.1.5). To simplify the modelling process and reduce the computational time needed, we did not consider the small portion of (200) and (220) surfaces detected by XRD. However, for future studies, it is helpful to consider the adsorption energies on these surfaces as well, as they may potentially influence the adsorption capacity of the overall system.

The DFT-calculated C and O adsorption energies and the most stable adsorption sites for each material are summarised in Table 4-5, the numbering system of the adsorption sites is detailed in the methodology section. The results showed that the C and O atoms tend to adsorb on the three-fold hollow sites. This is due to the stable geometry formed by the bonding between the adsorbate and the three surface atoms [38,39]. It is also observed that the change in adsorption energy of the bimetallic species is not strictly proportional to their composition. The C and O adsorption energies of both Ni_3Cu_1 and Ni_1Cu_1 are similar to pure Ni, whereas by increasing the concentration of Cu to 75 at.% (i.e. Ni_1Cu_3), the adsorption energies also increased. The same phenomenon was also reported by Alvarez-Garcia et al. [40], where the adsorption energies of CO_2 on Cu_3M_1 , Cu_1M_1 , and Cu_1M_3 (M = Ni, Pd, and Pt) were found to be very close or even higher than their monometallic components. This was attributed to the formation of bimetallic alloys and the synergistic effect between the two elements.

Table 4-5 C and O adsorption energies on Ni(111), Cu(111) and the bimetallic Ni-Cu surfaces.

Surface	Most stable C adsorption site	C adsorption energy (eV)	Most stable O adsorption site	O adsorption energy (eV)
Ni(111)	4. HCP	-7.86	3. FCC	-5.36
Cu(111)	3. FCC	-5.89	3. FCC	-4.70
Ni ₃ Cu ₁ (111)	3.2 FCC	-7.85	3.1 FCC	-5.31
Ni ₁ Cu ₁ (111)	4.2 HCP	-7.74	3.2 FCC	-5.28
Ni ₁ Cu ₃ (111)	4.2 HCP	-6.95	3.2 FCC	-5.03

To better understand and visualize the influence of adsorption energies on the catalytic activity of the materials, the three Ni-Cu bimetallic catalysts are plotted against the volcano plot obtained from the microkinetic modelling of the SMR process. The turnover frequency (TOF) of H₂ production was calculated by the MKM and illustrated as a function of the C and O adsorption energies (Figure 4-10), allowing for the fast qualitative comparison between different materials. A higher TOF (coloured in red) signifies a higher catalytic activity and metals such as Rh, Ni, Pd, and Pt are shown to be more active than Fe, Cu, and Au. The three bimetallic Ni-Cu catalysts were then plotted against the volcano plot based on their adsorption energies. As the adsorption ability of Ni₃Cu₁ and Ni₁Cu₁ towards the C and O atoms is very close to that of pure Ni, the TOF of both materials was predicted to be approximately 10⁻² s⁻¹ under the given conditions, which is at a similar level as monometallic Ni and Rh. This further confirmed the experimental observations mentioned in section 4.3.2. On the other hand, Ni₁Cu₃ has a relatively higher C adsorption energy (therefore lower carbon adsorption ability) compared to Ni₃Cu₁ and Ni₁Cu₁. Although a higher C adsorption energy means that carbon-containing species (e.g. CO and CO₂) can detach from the catalyst surface more easily, it also impedes the adsorption and decomposition of carbon-containing reactants. As CH₄ decomposition is generally agreed to be the rate-determining step in the SMR process, especially on Ni-based surfaces [41,42],

the relatively low TOF of 10^{-3} s^{-1} predicted for Ni_1Cu_3 is potentially due to its high C adsorption energy.

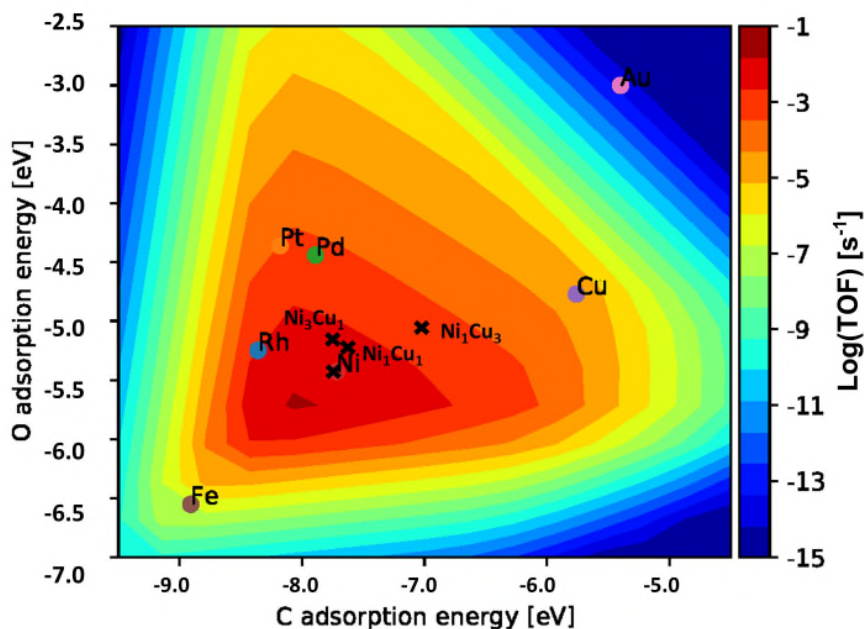


Figure 4-10 TOF of H_2 production as a function of C and O adsorption energies.

4.4 Conclusions

In this work, the performance of bimetallic Ni-Cu/ Al_2O_3 catalysts with different Cu loading (2.5, 5, and 7.5 wt.%) was evaluated under both SMR and SESMR conditions, and compared with the conventional Ni/ Al_2O_3 catalyst. Results from the SMR tests showed that all three bimetallic catalysts achieved higher methane conversion compared to Ni/ Al_2O_3 . The enhancement is most significant at 800 °C, with a methane conversion of approximately 90% achieved by $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$. The amount of coke formed on the used bimetallic catalysts was also found to decrease as Cu loading increased. The promoting effect of Cu on the catalytic activity and stability of the catalysts was attributed to its enhancing ability towards the WGS reaction and the synergistic effect between Ni and Cu in the binary alloy system. The formation of Ni-Cu alloy was confirmed by XRD analysis, the characterization of the catalysts also showed the even dispersion of both active metals within the highly porous alumina support, which contributed to the coke resistance of the bimetallic materials. The addition of the CO_2 sorbent

was found to enhance methane conversion by approximately 20%, compared with SMR under the same reaction temperature. However, hydrogen purity was found to decrease as temperature increases as CO₂ absorption is an exothermic process. A reaction temperature of 700 °C was considered to be optimal with the highest methane conversion of 96% achieved by Ni₃Cu₁/Al₂O₃ and Ni/Al₂O₃.

The experimental observations were supported by ab initio DFT calculations of the carbon and oxygen adsorption energies on the (111) surface of the mono and bimetallic catalysts. Both Ni₃Cu₁(111) and Ni₁Cu₁(111) showed similar adsorption abilities compared to the pure Ni(111) surface. The relatively low catalytic activity of Ni₁Cu₃ is potentially due to its lower carbon adsorption ability, which negatively affects the rate-determining methane decomposition reaction step. The relative catalytic activity of the three bimetallic catalysts and the two monometallic counterparts was also visualized using a microkinetic model of the SMR reaction. Ni₃Cu₁, Ni₁Cu₁ and Ni exhibited the highest hydrogen TOF (therefore highest catalytic activity), which is consistent with the experimental results.

In conclusion, the bimetallic Ni-Cu catalysts were found to be promising alternatives to the conventional Ni-based catalysts. A detailed techno-economic study can be carried out in the future to further investigate the cost of large-scale Ni-Cu catalyst production. It is also recommended that long-term SMR tests be carried out, potentially with the presence of sulphur species in the feed stream, to evaluate the long-term stability and coke and sulphur resistance of the catalysts.

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5 High throughput screening of sulphur-resistant catalysts for steam methane reforming

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Abstract

The catalytic activity of bimetallic catalysts for the steam methane reforming reaction has been extensively studied previously. However, the performance of these materials in the presence of sulphur-containing species is yet to be investigated. In this study, we propose a novel process aided by machine learning and microkinetic modelling for the screening of sulphur-resistant bimetallic catalysts. Firstly, various machine learning models were developed for the rapid prediction of atomic adsorption energies (C, H, O, and S) on bimetallic surfaces. Easily accessible physical and chemical properties of the metals and adsorbates were used as the input features. The Ensemble model achieved the best performance with an R^2 value of 0.74. A microkinetic model was then built based on the elementary steps of steam methane reforming. Finally, the microkinetic model, together with the atomic adsorption energies predicted by the Ensemble model was used to screen over 500 bimetallic materials. Four Ge-based alloys (Ge_3Cu_1 , Ge_3Ni_1 , Ge_3Co_1 , and Ge_3Fe_1) and the Ni_3Cu_1 alloy were identified as promising and cost-effective sulphur-resistant catalysts.

Keywords:

Sulphur-resistant catalysts; Machine learning; Microkinetic modelling; Catalyst screening; Steam methane reforming; Hydrogen production

5.1 Introduction

Steam methane reforming (SMR) is the most widely used process for syngas production. In this process, steam and methane react in the presence of a catalyst to

produce a mixture of carbon monoxide, carbon dioxide, and hydrogen. Although currently, most commercial SMR catalysts are supported nickel-based materials, extensive research on bi/polymetallic catalysts has been carried out with the aim of enhancing the overall catalytic activity and material stability [1–3]. However, the feed stream employed in most experimental studies is a mixture of pure methane and steam, and the effect of impurities on the performance of the catalysts was often not considered. One of the most important sources of methane – natural gas – usually contains sulphur in the form of thiophenes, mercaptans and sulphides [4]. Sulphur components are known to be poisonous to metallic catalysts, reducing the life of commercial catalysts to only months or weeks when ppm levels of sulphur impurities are present in the feed gas [5]. Catalyst poisoning by sulphur usually takes place through the following processes [6]:

- Active site blockage: an adsorbed sulphur atom may physically block a three- or four-fold adsorption site.
- Adsorption energy modification: the chemical bond between the sulphur atom and its neighbouring atom(s) can modify their ability to adsorb the reactant molecules and dissociate the product molecules.
- Restructure of the catalyst surface: strongly adsorbed sulphur atoms can modify the surface structure and properties of the catalyst.

Adding a second metal, either as a promoter or as the second element to form an alloy with the base metal, is a commonly used method to improve the overall sulphur resistance of the catalyst. A novel Ni-Fe-based catalyst with a core-shell structure was tested by Tsodikov et al. [7] and its catalytic activity remained unaffected as the concentration of H₂S in the system increased from 5 to 30 ppm. Wang et al. [8] reported that the bimetallic Ni-Re/Al₂O₃ catalyst achieved a high methylcyclohexane conversion rate of 93% during the steam reforming process in the presence of 20 ppm sulphur, whereas the monometallic Ni/Al₂O₃ catalyst quickly deactivated. Gaillard et al. [9] tested the stability of Ni-Mo/Al₂O₃ under long-term dry methane reforming conditions in the presence of 50 ppm H₂S and concluded that the bimetallic catalyst showed a better performance compared with the Ni or Mo counterparts. Similarly, Saha et al. [10] reported that the addition of Co enhanced the stability of Ni/Al₂O₃ for the dry reforming of biogas containing 100 ppm H₂S.

Apart from the experimental testing of the materials of interest, high throughput screening aided by Machine Learning (ML) has also been applied in the rapid scanning of large material databases to find materials that may perform well based on their physical and chemical characteristics [11,12]. Liu et al. [13] developed a ML model to predict the adsorption energies of C and O atoms on bimetallic surfaces. With the help of a Microkinetic Model (MKM) of the SMR reaction, they used the predicted adsorption energies to scan through over 5,000 materials and identified 48 promising candidates with high SMR activity. A similar approach was adopted by Saxena et al. [14] where the C and O adsorption energies on Cu-based bimetallic surfaces were predicted by ML and used in a MKM for ethanol decomposition. Liu et al. [15] used ML-predicted C and O adsorption energies and the MKM for methanol synthesis, methanation and SMR to scan over 1,300 alloys in search of highly active catalysts. All of these studies were only focused on the activity of the catalysts and the energetics of carbon- and oxygen-containing species. However, as mentioned previously, the stability of the materials is also an important aspect to consider, in particular their resistance to sulphur. It is therefore of interest to employ this integrated “ML + MKM” method for the rapid screening of sulphur-resistant catalysts.

In this study, various ML algorithms were used to predict the adsorption energies of C, O, H, and S atoms on monometallic and bimetallic surfaces, using readily available physical and chemical properties as input features, and Density Functional Theory-calculated adsorption energies as the target values. A microkinetic model of the SMR reaction was developed and together with the ML-predicted energies, these were used for the scanning of over 500 bimetallic alloys. To the best of the authors’ knowledge, this is the first-ever attempt at the systematic high throughput screening of sulphur-resistant SMR catalysts.

5.2 Methodology

5.2.1 Density Functional Theory

All DFT-based calculations in this work were carried out using the Quantum Espresso software [16]. The core electrons were described using the Kresse-Joubert Projector Augmented Wave (PAW) method. The exchange correlations were described using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [17]. The cutoff energies for the wave function and charge were set

to be 25 and 250 Ry, respectively. The convergence criteria for force and energy were set to be 0.025 eV/Å and 10^{-5} eV, respectively. All catalysts were simulated by a four-layer $p(2 \times 2)$ slab model, with the top two layers and the adsorbate relaxed, and the bottom two layers fixed. The k-point grid was set to be $3 \times 3 \times 1$ for the sampling of the Brillouin zone. A 10 Å vacuum was added to separate the two neighbouring layers in the z-direction. The adsorption energy (E_{ads}) is calculated as below:

$$E_{ads} = E_{ads*slab} - E_{ads} - E_{slab}$$

Where $E_{ads*slab}$ is the total energy of the slab with the adsorbate, E_{ads} the total energy of the gas phase adsorbate, and E_{slab} the total energy of the clean slab.

Adsorption on the following close-packed surfaces was considered: [111] for face-centred cubic systems (e.g. Ni, Cu, Rh, all bimetallic systems, etc), [110] for body-centred cubic systems (e.g. Fe, Nb, Mo, etc), and [0001] for hexagonal close packing systems (e.g. Co, Zn, Ru, etc). In the case where multiple adsorption sites are available, the site with the lowest adsorption energy was chosen, as it indicates the most stable geometry.

All gas phase species were modelled by placing the molecule in a cube with the lattice parameters of $a = 20$ Å, $b = 20.5$ Å, $c = 21$ Å. The k-point grid was set to be $1 \times 1 \times 1$ for all gas phase calculations.

5.2.2 Machine Learning

5.2.2.1 Database construction

The database used for the ML model training consists of DFT-calculated adsorption energies of C, H, O, and S on 23 monometallic and 12 bimetallic surfaces (a total of 140 data points). Each pure metal is represented by a set of 12 features, including fundamental properties (e.g. group, atomic number, covalent radius, etc) and surface-related properties (e.g. surface free energy, work function, etc). Each alloy ($M1_xM2_y$) is represented by the features of its components (12 features of M1 plus 12 features of M2) and the ratio of x:y to account for the concentration of each component within the binary system. For monometallic inputs, the ratio was considered as 1. The adsorbates (C, H, O, and S) are represented by a set of 9 properties, including group, atomic number, first ionization potential, etc. The complete input database, including

numerical values of the features and the adsorption energies, can be found in Supplementary Information (0).

5.2.2.2 ML algorithms

Different ML algorithms were used for the prediction of C, H, O, and S adsorption energies, including Linear Regression (LR), Ridge Regression (RR), K-Nearest Neighbours Regression (KNN), Random Forest Regression (RFR), Extra Trees Regression (ETR), Gradient Boosting Regression (GBR), Support Vector Regression (SVR), Light Gradient Boosting Machine (Light GBM), Artificial Neural Network (ANN), and Ensemble learning.

The ANN model was implemented using Keras with a TensorFlow backend [18]. All other algorithms were implemented using the open-source ML library Scikit-Learn [19]. The dataset was randomly split into training (80%) and testing (20%) subsets. The accuracy of the models was evaluated based on the Mean Squared Error (MSE), Mean Absolute Error (MAE), and coefficient of determination (R^2). The evaluation metrics were calculated using the following equations:

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad \text{5-1}$$

$$\text{MAE} = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i| \quad \text{5-2}$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad \text{5-3}$$

Where n is the number of samples, y_i the DFT-calculated value of the sample i , $\hat{y}_i$ the predicted value of sample i , and the $\bar{y}$ the average of the DFT-calculated values.

Tuning of the hyperparameters was conducted using the 5-fold cross-validation (CV) method via GridSearch. The range of hyperparameters tested for each model during the tuning process is summarized in Table 5-1. Feature importance study was carried out using Recursive Feature Elimination (RFE). The features were ranked based on their importance and the ones that did not contribute significantly to the model performance were eliminated from the model.

Table 5-1 Range of hyperparameters tested for ML models.

ML algorithm	Hyperparameters
RR	Alpha = [0.5, 0.75, 1, 1.25, 1.5]
KNN	N neighbours = [1, 3, 5, 7, 8, 9] Weights = [uniform, distance]
RFR	Max depth = [25, 50, 75, 100] N estimators = [500, 1000, 1500, 2000]
ETR	Max depth = [25, 50, 75, 100] N estimators = [500, 1000, 1500, 2000]
GBR	Max depth = [25, 50, 75, 100] N estimators = [500, 1000, 1500, 2000] Learning rate = [0.01, 0.03, 0.05, 0.07]
SVR	Kernel = ['linear', 'rbf'] C = [0.1, 1, 10]
Light GBM	Max depth = [25, 50, 75, 100] N estimators = [500, 1000, 1500, 2000] Learning rate = [0.01, 0.03, 0.05, 0.07]
ANN	Number of layers = [2, 3, 4, 5] Dropout rate = [0.1, 0.2, 0.3, 0.4, 0.5] Learning rate = [0.01, 0.001, 0.005] Epochs = [100, 200, 300, 400, 500]

5.2.3 Microkinetic Modelling

The MKM was implemented with the descriptor-based analysis tool CatMAP [20], using the methodology described in our previous work [21]. CatMAP provides a flexible and automated framework for constructing descriptor-based microkinetic analyses, and the production rate of a defined system is calculated as the turnover frequency (TOF). The model of the SMR reaction was developed based on seven pure transition metals which have been widely used as catalysts or catalyst promoters for the SMR reaction – Rh, Ni, Cu, Fe, Pd, Pt, and Au. DFT-calculated energies were used as the model input, together with energetics calculated and estimated using the unity bond index-quadratic exponential potential (UBI-QEP) method and the Brønsted–Evans–Polanyi (BEP) relationship. These methods have been widely used in the field of

surface adsorption and are capable of yielding accurate results without the need for time-consuming first-principle-based calculations [21,22]. Detailed information on the input data is available in Supplementary Information. The reaction pathway and elementary steps considered for the model for SMR are illustrated in Figure 4-2, which included CH₄ and H₂O dehydrogenation, CO formation through multiple routes (COH* and HCO* dehydrogenation and CO* desorption), and interaction between various intermediate species. It should be noted that although the actual reaction mechanism of SMR is more complicated with other intermediate species involved, the simplified mechanism described in this work is accurate enough to describe the overall trend of the reaction without overly high computational demand. The reaction conditions were set to be 1,073 K and 1 bar, with a H₂O : CH₄ ratio of 3, which are the typical conditions used for the SMR process. The Shomate equation and frozen adsorption were used to model the gas-phase species and the adsorbates, respectively. The Shomate parameters for the gases were obtained from the NIST website [23].

To conclude the methodology used in this work, a combined “ML + DFT + MKM” approach was employed, including the following steps:

- DFT calculations of C, O, H, and S adsorption energies were carried out for 35 metallic surfaces.
- Part of the DFT-calculated energies were used for the construction of the microkinetic model.
- All DFT-calculated energies were used as the input dataset for the ML models.
- The best-performing ML model was used to predict the C, O, H, and S adsorption energies on over 500 bimetallic surfaces.
- The 500+ bimetallic materials were screened based on results from the microkinetic model.

A schematic diagram of the methodological approach employed is provided in Figure 5-1.

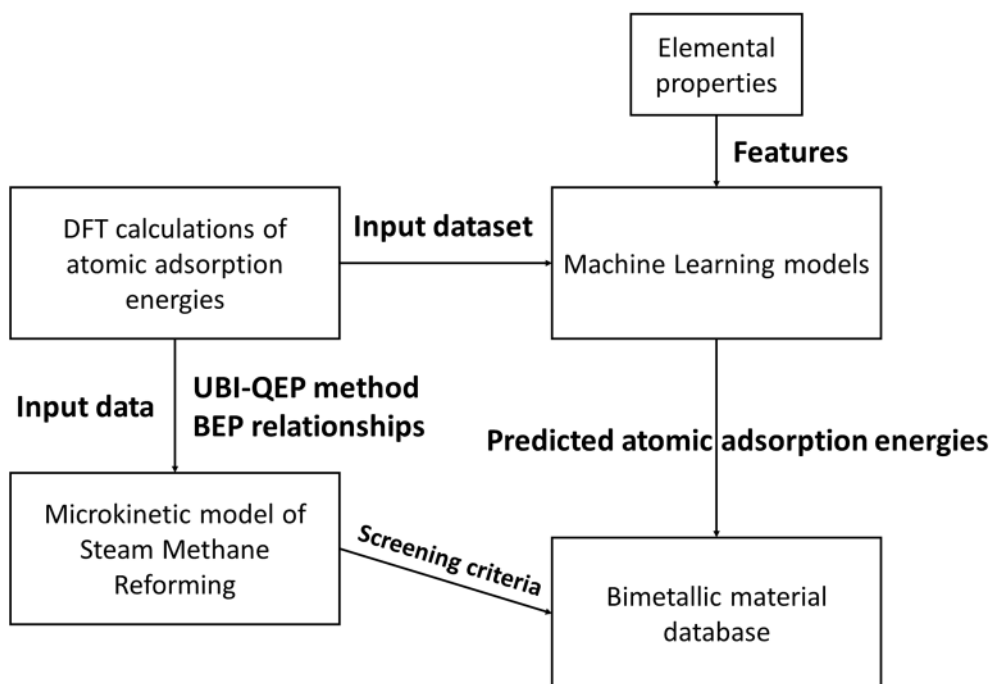


Figure 5-1 Schematic diagram of the "ML + DFT + MKM" approach.

5.3 Results and discussion

5.3.1 Machine Learning models

5.3.1.1 Hyperparameter tuning

Hyperparameter tuning is an essential step in the ML model development process – it ensures that the model developed is complex enough to capture the characteristics of the input features, but at the same time not too complex to cause overfitting. The types of hyperparameters tuned and the range of values before and after the tuning process are summarized in Table 5-1 and Table 5-2, respectively.

Table 5-2 Optimized hyperparameters for each ML algorithm.

ML algorithm	Hyperparameters
RR	Alpha = [1.25]
KNN	N neighbours = [5]; Weights = [distance]
RFR	Max depth = [75]; N estimators = [2000]
ETR	Max depth = [100]; N estimators = [1500]

GBR	Max depth = [100]; N estimators = [1000]; Learning rate = [0.07]
SVR	Kernel = ['rbf']; C = [10]
Light GBM	Max depth = [25]; N estimators = [500]; Learning rate = [0.01]
ANN	Number of layers = [3]; Dropout rate = [0.2]; Learning rate = [0.001]; Epochs = [500]

5.3.1.2 Feature selection and engineering

Feature selection is an important step in the ML model development process. The features selected should be unique in representing the geometric and electronic structure of a specific adsorption site. Commonly used features can be divided into three main categories:

- Elemental properties including atomic number, mass and radius; ionic potential; electronegativity, etc. These properties only depend on the host-metal atom and can be easily obtained from literature or the periodic table.
- Electronic properties including *d*-band features such as centre, filling, width, skewness, kurtosis, etc [25–27]. These features are more complex than basic elemental properties and usually require single-point DFT calculations to obtain.
- Geometric properties including local electronegativity and effective coordination number [28,29]. These features are usually used when the adsorption energies on different adsorption sites are compared. This is not the case for this study, as the most stable adsorption sites have been pre-selected during the DFT calculation process.

In this work, only the elemental properties were considered as input features, as they are readily available and have been shown to produce sufficiently accurate results [30–33]. As mentioned in the methodology section, 12 features for each metal, 9 features for each adsorbate, and the ratio between the two metals were selected as the initial input features. This means that 21 features were used to represent one atomic adsorption energy on a monometallic surface and 34 features for a bimetallic surface. However, as we were dealing with a relatively small database (less than 200 data points in the input database), a large number of input features may lead to

overfitting. It is therefore necessary to identify and eliminate the features with diminished importance, which may contribute to inaccuracies during the prediction process.

Feature importance was evaluated using the Ensemble model with tuned hyperparameters, and the relative importance of each feature is presented in Figure 5-2. The Gini importance parameter was used to evaluate the importance of each feature:

$$\text{Gini importance} = \sum_{t \in T} p(t) \times (1 - \sum_{i=1}^C [p(i|t)]^2) \quad 5-4$$

Where t is the set of all nodes that use the given feature, $p(t)$ the proportion of samples reaching the node t , and $p(i|t)$ the proportion of class samples i at node t .

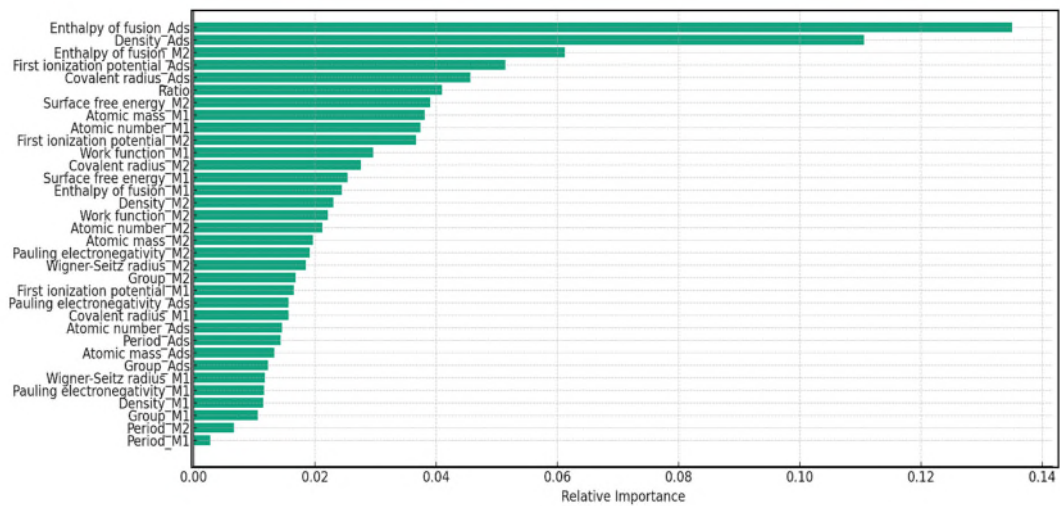


Figure 5-2 Relative feature importance for the Ensemble model.

The result shows that the properties of the adsorbate contribute most significantly to the prediction, with four out of the top five features being the enthalpy of fusion, density, first ionization potential, and covalent radius of the adsorbate. Properties of the metals, including enthalpy of fusion, surface free energy, atomic mass, atomic number, and first ionization potential were also found to have relatively high importance. This is consistent with the trend observed by Nayak et al. [34], where the most important features are first ionization potential and enthalpy of fusion for the adsorbate, and group, surface free energy, and enthalpy of fusion for the surface. In order to enhance the overall accuracy of the ML prediction, only the top 12 features were included for the models. This ensures that the predictions are made based on

the most informative and pertinent features, and therefore deliver the most precise predictions of the adsorption energies.

The linear relationship between each of the 11 features (top 12 most important features, excluding “ratio”) and the target value – adsorption energy – was quantified by the Pearson correlation coefficient. The result is presented in the form of a heatmap in Figure 5-3. The first ionization potential of the adsorbate exhibits the highest positive correlation with a correlation coefficient of 0.42, which again confirms the significance of the adsorbate’s electronic properties. This is consistent with the previous observations that higher charge transfer leads to lower adsorption energy [35]. A higher ionization potential represents a lower probability for charge transfer and therefore higher adsorption energy. The density of the adsorbate exhibits the most substantial negative correlation, with a correlation coefficient of -0.5. This is in line with the general trend that heavier atoms tend to have lower adsorption energies. For instance, the adsorption energies of carbon on transition metal surfaces are usually in the range of -5.0 to -10.0 eV, whereas the adsorption energies of hydrogen are in general between -2.0 and -5.0 eV.

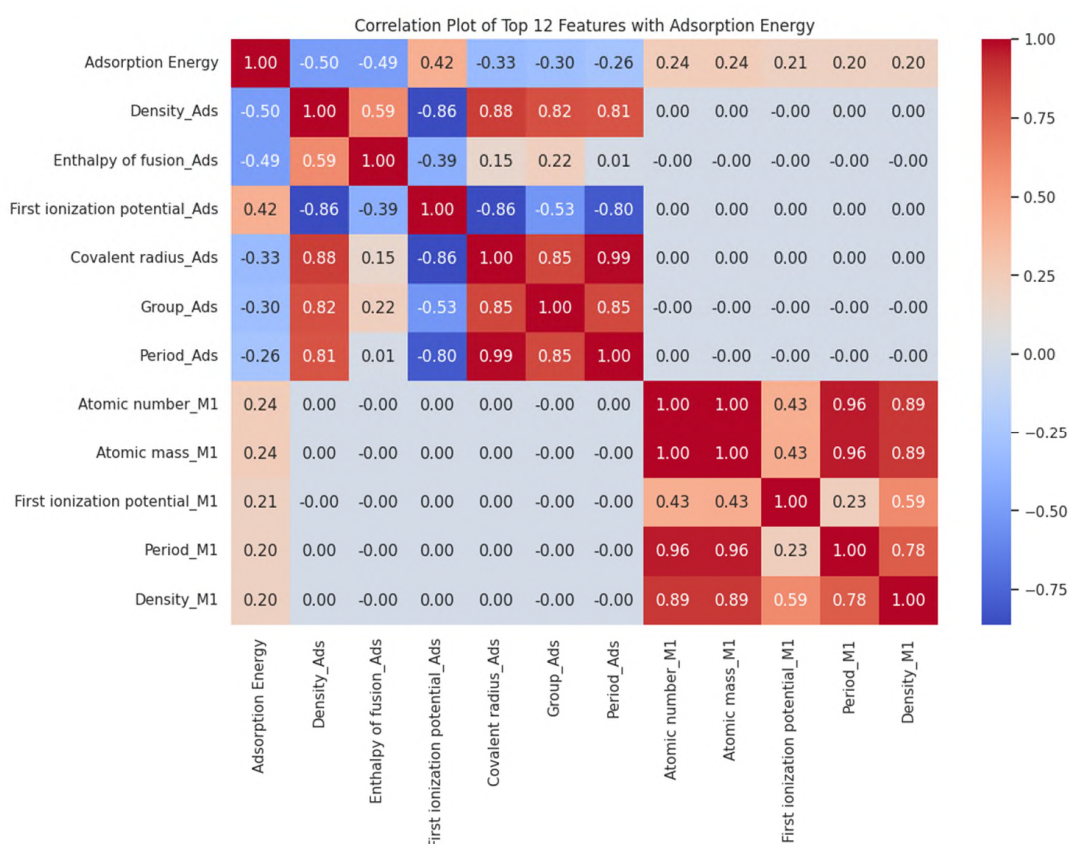


Figure 5-3 Correlation heatmap for the adsorption energy with the top 11 features.

5.3.1.3 Model performance evaluation

Following the model optimization process, all ML models were reprogrammed using the top 12 features and the tuned hyperparameters. The evaluation metrics obtained for each model, including train and test MSE, MAE and R^2 , are summarized in Table 5-3. The regression plots of the three best-performing models (Ensemble, ANN, and SVR) and the low-performing KNN model are presented in Figure 5-4. The Ensemble model exhibited the best overall performance, with the highest test R^2 of 0.74, a test MSE of 1.45, and a test MAE of 0.76. This was followed by the ANN and SVR models, with test R^2 values of 0.71 and 0.70, respectively. On the other hand, the KNN model produced the least optimal results, with the lowest test R^2 of 0.48 and the highest MSE of 3.42. It can be observed from the regression plot (Figure 5-4 (d)) that the KNN model presented a random pattern of predictions with dispersed training and testing results. This is possibly due to the localized focus of the KNN model, which does not suit the complexity of the dataset.

The Ensemble, ANN, and SVR models demonstrated their ability to capture the underlying patterns of the dataset effectively. The models are able to produce accurate predictions for adsorption energies in the range of -2.0 to -8.0 eV. However, the models faced challenges when encountering extreme values (i.e. adsorption energies higher than -2.0 eV and lower than -8.0 eV), leading to an increase in the MSE values. This is not uncommon, as the performance of ML models is sometimes limited when the values deviate significantly from the dataset's central tendencies. As the adsorption energies of the C, H, O, and S atoms on most transition metal surfaces usually reside in the range of -2.0 to -8.0 eV, it is physically unlikely to further increase the amount of input data outside this range.

It should also be noted that the accuracy of a ML model relies heavily on the size of the input database. The performance of the models developed in this work can be further optimized by conducting additional DFT calculations to increase the number of input data points. This is further addressed in the "Limitations and future outlook" section, where suggestions for further optimization and improvement of the model are given.

Table 5-3 Performance evaluation metrics of the ML models.

Model	Train			Test		
	MSE	MAE	R ²	MSE	MAE	R ²
Ensemble	0.37	0.38	0.92	1.45	0.76	0.74
ANN	0.42	0.43	0.91	1.93	0.79	0.71
SVR	0.44	0.40	0.91	1.19	0.80	0.70
RFR	0.32	0.39	0.93	1.96	0.81	0.69
Light GBM	0.92	0.68	0.78	2.68	1.23	0.59
ETR	0.93	0.72	0.76	2.72	1.27	0.58
GBR	0.98	0.72	0.75	2.78	1.31	0.57
RR	1.79	0.92	0.63	2.90	1.34	0.56
LR	1.44	0.79	0.70	1.74	1.41	0.52
KNN	1.84	0.93	0.61	3.42	1.56	0.48

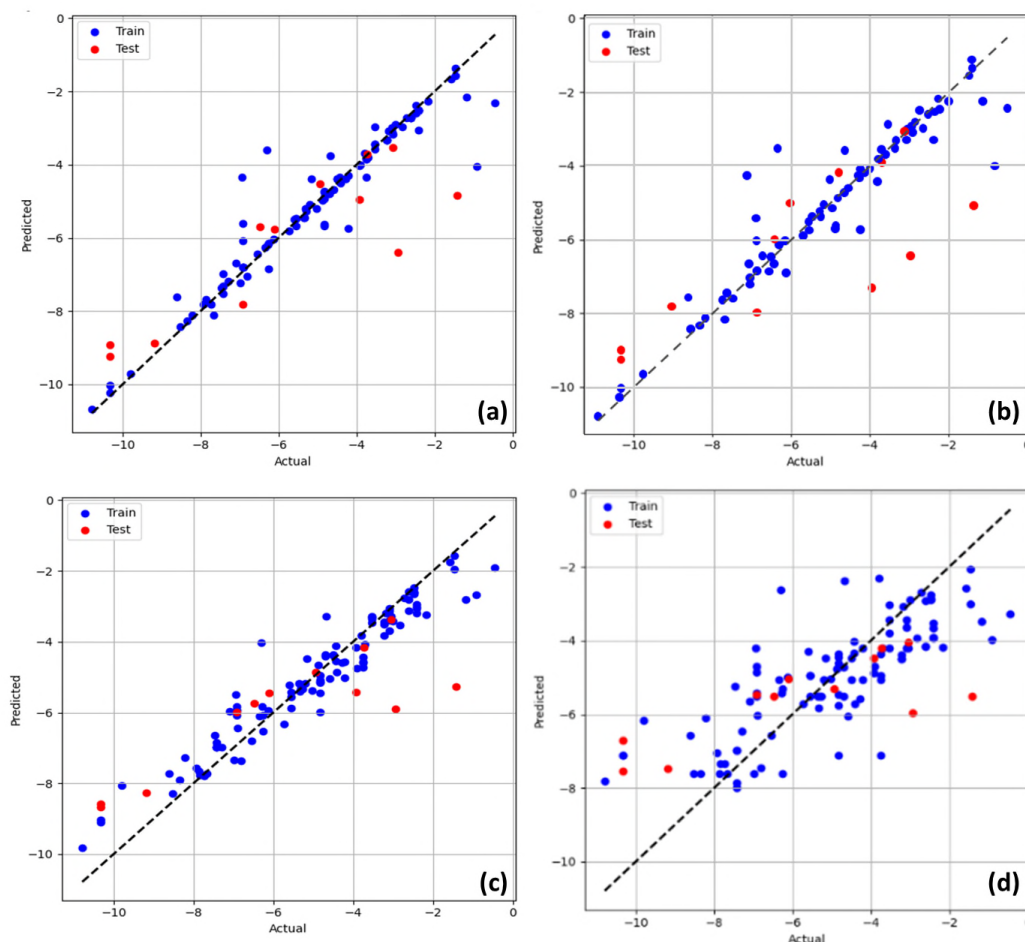


Figure 5-4 Regression plots for the three best-performing models (a) ER, (b) ANN, (c) SVR, and (d) the low-performing KNN model.

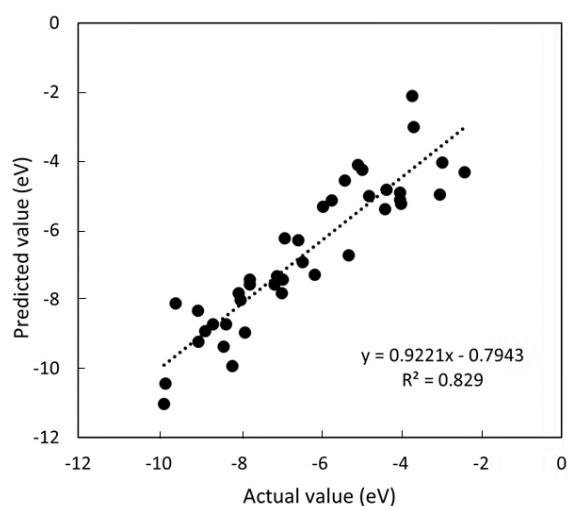
5.3.1.4 Model validation

Model validation is a crucial step in the process of developing a ML model as it ensures the reliability, accuracy, and generalization capability of a predictive model. Proper validation also helps in identifying and addressing biases, errors, and shortcomings of the model, thus enhancing its performance. In this section, the Ensemble Learning model developed previously is validated using 40 unseen data points (four adsorption energies for each of the 10 bimetallic surfaces). The 10 bimetallic surfaces were selected randomly to ensure the representability of the validation data. However, the number of Ni-containing species was manually increased to 4 as Ni is the most commonly used SMR catalyst. Among the 10 unseen bimetallic surfaces, five bimetallic M_1M_2 surfaces with an $M_1:M_2$ ratio of 1:1 were included to evaluate how well the model performs for materials with different surface configurations. The “actual” C, O, H, and S adsorption energies of the 10 bimetallic alloys, which formed the validation

dataset, were obtained using DFT calculations. The “actual” and predicted values are summarized in Table 5-4, and the corresponding regression plot is presented in Figure 5-5. As can be seen from the table and the regression plot, the model achieved satisfying results for the validation dataset containing 40 unseen data. The R^2 value of the validation dataset reached 0.829, which is higher than the R^2 of 0.74 obtained by the testing dataset using the Ensemble model. This can be explained by the range of unseen data used for validating the model. As mentioned in the previous section, the Ensemble model performed well for adsorption energies in the range of [-4.0 eV, -0.8 eV], as most training data resides in this range. As the adsorption energies of the four types of atoms considered in this study (C, O, H, and S) seldomly fall outside the range of [-4.0 eV, -0.8 eV], the accuracy of the model is considered acceptable. As most of the unseen data used for the validation process is located within this range, the model achieved a higher R^2 value. In conclusion, the Ensemble model is proven to be capable of producing accurate results for the prediction of atomic adsorption energies and is therefore subsequently used for the screening process.

Table 5-4 Actual energies and predicted energies of the validation dataset.

	Carbon adsorption energy (eV)		Oxygen adsorption energy (eV)		Hydrogen adsorption energy (eV)		Sulphur adsorption energy (eV)	
Surface	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
Ni ₁ Cu ₁	-7.74	-7.56	-5.28	-6.72	-3.71	-2.11	-9.58	-8.11
Ni ₁ Fe ₁	-8.17	-9.92	-6.13	-7.29	-4.01	-5.12	-9.87	-11.02
Ni ₁ Ge ₁	-4.95	-4.25	-3.98	-5.23	-2.41	-4.31	-6.92	-7.43
Ru ₁ Sb ₁	-6.94	-7.82	-5.70	-5.13	-3.02	-4.96	-8.84	-8.91
Pt ₁ Zn ₁	-7.06	-7.32	-5.38	-4.56	-3.67	-3.01	-9.02	-8.32
Ni ₃ As ₁	-6.87	-6.23	-5.05	-4.10	-2.96	-4.03	-7.86	-8.95
Ag ₃ Bi ₁	-8.01	-7.82	-5.92	-5.32	-4.01	-4.91	-9.83	-10.43
Pd ₃ Ga ₁	-7.74	-7.43	-6.53	-6.28	-4.78	-5.01	-8.32	-8.72
Cu ₃ Sn ₁	-8.65	-8.72	-7.12	-7.56	-4.34	-4.82	-9.01	-9.23
Pt ₃ In ₁	-7.97	-8.02	-6.43	-6.92	-4.38	-5.38	-8.39	-9.37

**Figure 5-5 Regression plot of the validation dataset.**

5.3.1.5 Predicted adsorption energies

Following the model validation process, the best-performing ML model was applied to a list of bimetallic alloys, the adsorption energies of which were not all readily available. A total of 24 metal elements were considered and permuted with one another, which generated a set of over 500 ($24 \times 23 = 552$) bimetallic alloys. As mentioned in the model development section, one of the input features used for the ML model is the ratio of the two individual components within the binary system. By changing the numerical value of the “ratio” feature, the ML model is able to deal with a given binary alloy with any M1 or M2 concentration. In this work, we focused on bimetallic materials with a M1:M2 ratio of 3 (i.e. 75 mol.% of M1 and 25 mol.% of M2).

The predicted C, O, and S adsorption energies are visualized in a scatter plot (Figure 5-6). The complete list of predicted energies is available in Supplementary Information. The X and Y axis of the plot represent the C and O adsorption energies, respectively. The S adsorption energies are displayed using colour coding, where a darker blue colour represents a lower value (therefore more prone to S adsorption) and a lighter green represents a higher value (less prone to S adsorption). Based on previous research on the interaction between sulphur and transition metal-based catalysts [36,37], sulphur poisoning takes place through two main routes: the reversible adsorption of sulphur-containing species (at lower concentrations) and the irreversible chemisorption of sulphur due to the formation of metal sulphides. Therefore, having a higher value of S adsorption energy is in general favourable for the catalyst, as it allows for a more difficult adsorption and easier desorption of sulphur species. A trend that can be observed from the scatter plot is that materials with higher S adsorption energies tend to have higher C and O adsorption energies as well. However, unlike S adsorption energy, having higher C and O adsorption energies is not necessarily beneficial for the SMR reaction to take place. A material's catalytic activity for the SMR reaction is highly dependent on the C and O adsorption energies [13,38,39]. Based on the Sabatier principle [40], the binding abilities of the catalyst should be neither too strong for the products to desorb, nor too weak for the reactants to adsorb. It is therefore crucial to identify the materials which have high sulphur

resistance and at the same time, appropriate C and O adsorption abilities for good catalytic activity.

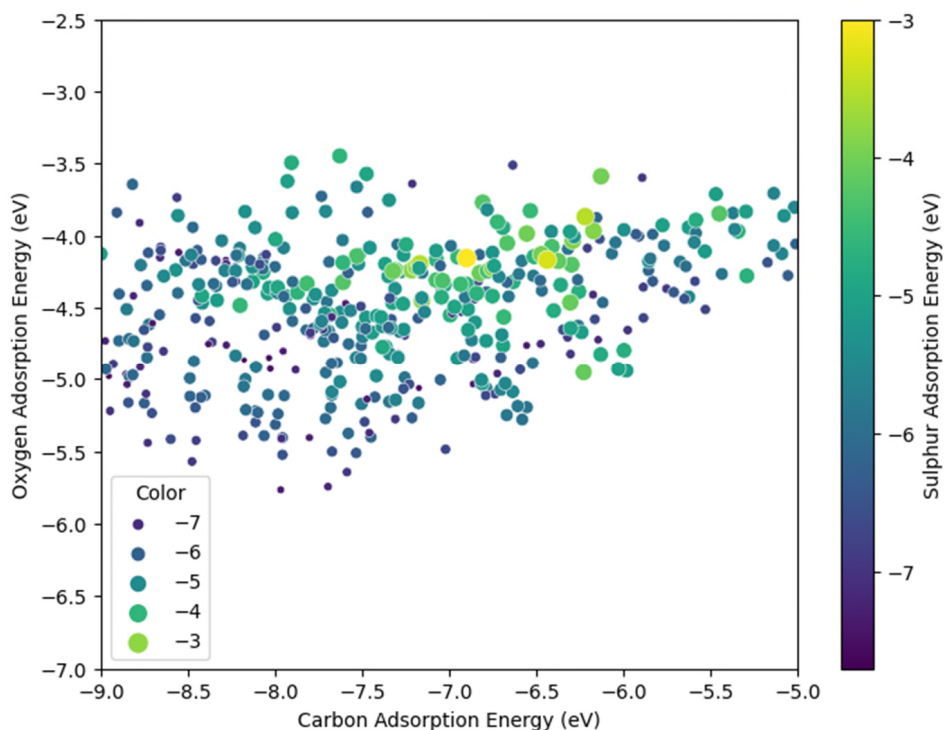


Figure 5-6 Scatter plot of C, O, and S adsorption energies of 500+ bimetallic catalysts. (Smaller circles with darker blue colour represent lower S adsorption energies, and bigger circles with light yellow colour represent higher S adsorption energies.)

5.3.2 Microkinetic Modelling and catalyst screening

In order to identify the optimal C and O adsorption energies, a MKM of the SMR reaction was developed and the results obtained are presented in the form of a “volcano plot” (Figure 5-7). The X and Y axis indicate the C and O adsorption energies, respectively. The colour of the contours indicates the TOF of the production of hydrogen, which is directly linked to the catalytic activity of the catalysts. The C and O adsorption energies of the seven pure metals are in the range of [-8.9, -5.5] and [-6.2, -2.9] eV. The activity trend of the materials is in the order of Rh>Ni>Pd≈Pt>Fe>Au, which is consistent with the general trend observed for these metals [41,42]. The boxed area in Figure 5-7 represents the region for the highest catalytic activity, the optimal C and O adsorption energies

were therefore identified to be C [-8.5, -7.0] eV, and O [-6.5, -5.0] eV. The database containing ML-predicted adsorption energies of the bimetallic alloys was then scanned through, and the materials that were located in the optimal range were considered to be highly active catalysts for SMR.

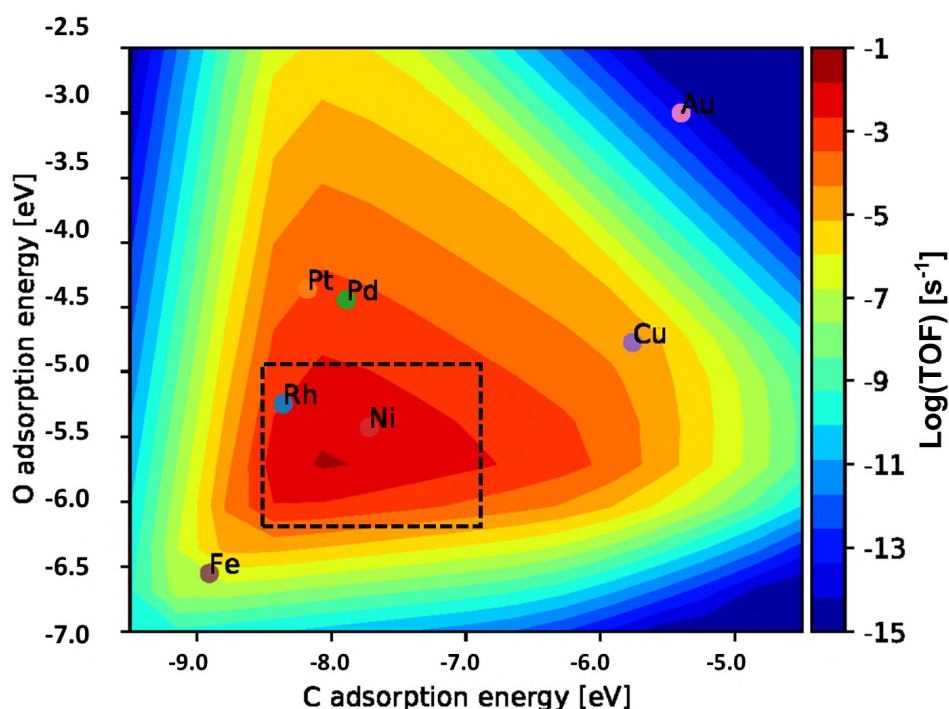


Figure 5-7 Volcano plot of the SMR model (boxed area: highest catalytic activity).

A total of 49 bimetallic alloys were identified as having the optimal C and O adsorption energies for the SMR reaction (Table S4). These candidates were then sorted based on their S adsorption energies, and the top ten materials with the highest S adsorption energy were considered the most promising sulphur-resistant SMR catalysts. Amongst the ten catalysts, we have identified one Tc-based alloy (Tc_3Ni_1), three noble metal-based alloys (Rh_3Co_1 , Rh_3Fe_1 , and Ru_3Cu_1), one Ni-based alloy (Ni_3Cu_1), and five Ge-based alloys (Ge_3Cu_1 , Ge_3Ni_1 , Ge_3Co_1 , Ge_3Pd_1 , and Ge_3Fe_1). Due to the carcinogenicity and radioactivity of Pd and Tc, Ge_3Pd_1 and Tc_3Ni_1 are not considered suitable candidates. Rh- and Ru-based materials have been proven to have excellent catalytic activity and coke resistance for SMR [43–45]. However, not as many studies have been carried out to investigate the sulphur resistance of these noble metal-based materials. A $\text{CeO}_2\text{-Al}_2\text{O}_3$ -supported Rh-Ni catalyst was reported to maintain a high conversion

of 95% for 72 h during the reforming process of a jet fuel containing 22 ppm sulphur [46,47]. This was attributed to the migration of S in RhS_x species to Ni in the close vicinity of Rh, due to the sulphur spillover effect. Ni-Cu-based bimetallic catalysts have been tested for various reforming processes [48–50] and have been proven to achieve enhanced activity compared to their individual Ni and Cu counterparts. However, no experimental evaluation of their sulphur resistance is currently available. Compared to transition metal-based catalysts, the use of Ge-based materials as catalysts is less common and their performance under steam methane reforming conditions is less well understood. Ge-based bimetallic catalysts have been tested for hydrogen production from ammonia borane [51] and hydrogenation of acetylene [52] and have shown enhanced activity and selectivity. Although no experimental validation is available, the sulphur-resistant ability of germanium may be attributed to its electronic structure. The electronic structure of sulphur is very similar to tetra-valent metals, including germanium, which has spare p -electrons in its outer shell next to a stable s -orbital. The interaction between the spare $4p$ electrons from sulphur and the metal atoms leads to the formation of metal sulphides [53]. It is therefore possible that the p -electrons from Ge act as a “placeholder” on the bimetallic surface and block the route for potential bond formation between sulphur and the other metallic elements.

5.3.3 Limitations and future outlook

In this section, we aim to provide an analysis of the proposed “ML + MKM” screening method and suggestions for further improvement. First of all, it is crucial to acknowledge the limitations of using a relatively small database in the context of ML. The quantity and quality of the input data has always been one of the greatest challenges when dealing with adsorption energy prediction, particularly due to the following reasons:

- Lack of data for a specific atom/molecule: C and O are two of the most studied atoms in the field of heterogeneous catalysis and information on their adsorption abilities is readily available from commonly used databases (e.g. Catalysis Hub [54], CatApp [55], etc). However, data on

sulphur adsorption energy is less accessible, DFT-based calculations are therefore usually inevitable.

- Lack of adsorption data on uncommon surfaces: Data available from the previously mentioned databases is usually focused on group VIII – XI metal elements only. DFT calculations are required to obtain information on metalloid surfaces or other uncommon transition/post-transition metal surfaces.
- Heavy computational burden: First-principle-based DFT calculations demand very high computational capacity and can be time-consuming. For instance, the computational time needed for a single adsorption energy calculation is approximately 100 minutes on 8 high-performance CPUs [14].

By increasing the size of the input database, it is possible to further improve the accuracy of the ML predictions. It is also recommended that more bimetallic alloys be added to the training base so that the models can better capture the full complexity and variability of the adsorption process on bimetallic surfaces. The MKM can also be improved by refining the reaction mechanism described in the model. For instance, the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) can be added as it takes place simultaneously with the SMR reaction under realistic experimental conditions. However, it should be noted that by increasing the number of reactions and intermediate species, more DFT calculations are consequently needed. It would also be interesting to utilize ML for other energy-related predictions. In this work, we used sulphur adsorption energy as a simple indicator of the material's sulphur-resistant ability. However, other parameters such as the activation barrier of the H_2S decomposition can also serve as accurate indicators. Similarly, the use of ML to predict these activation barriers instead of first-principle-based calculations will significantly reduce the resources and time required.

5.4 Conclusions

In this work, a combined “Machine learning + Microkinetic modelling” method was employed for the fast scanning of bimetallic sulphur-resistant catalysts. Different

ML algorithms were used to predict the atomic adsorption energy of C, H, O, and S using basic physical and chemical properties of the metallic elements and the adsorbates. Among all the ML models studied, the Ensemble learning, ANN, and SVR models achieved the best results ($MAE < 1$ and $R^2 \geq 0.7$). Results from the feature importance study demonstrated that elemental properties of the adsorbates contribute most significantly to the prediction, with enthalpy of fusion, density, first ionization potential, and covalent radius of the adsorbate being the most important features. Over 500 bimetallic alloys were considered as candidates, obtained by the permutation between 24 elements (including transition/post-transition metals and metalloids). The adsorption energies on these bimetallic surfaces were then predicted using the best-performing Ensemble learning model.

On the other hand, a microkinetic model was developed based on a simplified reaction mechanism of the SMR reaction, using both DFT-calculated energies and energetics obtained using the UBI-QEP method and BEP relationships. It is observed that having a carbon adsorption energy between -8.5 – -7.0 eV and an oxygen adsorption energy between -6.5 – -5.0 eV results in the highest catalytic activity for the SMR reaction. Using this range of optimal adsorption energies, the 500+ candidates were scanned and 49 were identified to be highly active catalysts. After excluding carcinogenic and radioactive elements, the following materials were concluded to be active SMR catalysts with the best sulphur-resistant ability: Ge_3Cu_1 , Ge_3Ni_1 , Ge_3Co_1 , Ge_3Fe_1 , Rh_3Co_1 , Rh_3Fe_1 , Ru_3Cu_1 , and Ni_3Cu_1 .

In conclusion, this paper presents the first attempt to systematically scan bimetallic catalysts with high sulphur-resistant abilities. Although further improvements are possible, the ML models provided satisfying results and the MKM greatly facilitated the scanning process. The method described in this work is also applicable to other chemical or pharmaceutical processes, where the scanning of large material databases is required.

5.5 References

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6 General discussion

In this chapter, a general discussion of the findings from this PhD study is provided, and the linkages between each chapter are explained.

6.1 General discussion

Hydrogen is expected to play a very important role in the future net zero system as it is seen as a promising alternative to fossil fuels in sectors including energy, transportation, heating, etc. The demand for hydrogen has grown more than threefold since 1975 [1] and continues to rise as the demand for clean energy rises. As an energy carrier, the extent to which hydrogen can be decarbonized is heavily dependent on its production pathway. Although green hydrogen produced from renewable sources (e.g. water electrolysis) and pink hydrogen produced using nuclear power are ideal options for producing hydrogen with low, zero, or even in some cases, negative carbon emission [2,3], these technologies are usually in the early stage and require further research and testing. Currently, hydrogen is nearly completely supplied from fossil fuels, with natural gas being the primary source. SMR is currently the most predominant hydrogen production pathway and is expected to remain so for the years to come. Although it is important to support the research and development of hydrogen from renewable sources, it is also of interest to continue the optimization of the SMR process, with the aim of a complete transition to blue hydrogen in the near future.

The aim of this work is, therefore, to investigate the application of bimetallic catalysts for the SMR process, as well as SESMR, a novel technology that integrates conventional SMR with simultaneous in-situ CO₂ capture. Although SMR is a well-established technology with decades of commercial applications, some aspects of it are still subject to perfection. Efforts have been made in the field of reactor design and novel reactor types [4], renewable energy supply for the process [5], and reaction conditions optimization [6,7]. However, the search for efficient and stable catalysts has always been the top focus of researchers. Monometallic catalysts supported on porous materials have been extensively studied previously [8]. Although noble metal-based catalysts showed unbeatably

high activity and stability, they are usually limited by their price and scarcity. Other transition metal-based materials (e.g. Ni- or Co-based) are therefore considered to be more favourable and have therefore been more widely applied in commercial SMR processes.

The addition of a second metal to the conventional Ni- or Co-based catalysts is a commonly used method to optimize the overall performance of reforming catalysts. Recent advances in bimetallic catalysts for dry methane reforming [9–11] and the reverse SMR process (CO methanation) [12] have been summarized and reviewed. This was the motivation for conducting a comprehensive literature review on bi/polymetallic catalysts for SMR, which was presented in Chapter 2. Ni-based catalysts accounted for more than half of all literature considered in the review, as nickel has been extensively proven to be highly efficient for SMR. Ni-based catalysts can be further divided into three main categories, namely, Ni promoted by noble metals, non-noble metals, and metalloids, respectively. Unsurprisingly, Ni catalysts promoted by noble metals (including Ru, Rh, Ir, Pt, and Pd) exhibited optimal performance with high methane conversion and hydrogen yield. They also excel in long-term stability and carbon resistance tests. On the other hand, although Au and Ag were found to be excellent promoters for enhancing carbon resistance, this was usually at the expense of their catalytic activity. The promoting effect of non-noble metals, including Fe, Co, Cu, Zr, La, Mo, and Re has also been studied and can be categorized into two main types – promotion of stability (namely carbon and sulphur resistance) due to alloy formation and promotion of the morphological properties through surface area, metal dispersion, and reducibility enhancement. The application of metalloid elements as promoters is less common. Silicon is usually used in its oxide or carbide form as the catalyst support, whereas Sn and B form an alloy with Ni and improve its long-term stability. Apart from the experimental studies, numerical studies were also taken into account in the literature review. Several bimetallic materials (Ni_3Sn_1 , Ni_3Sb_1 , Ni_3Ge_1 , Ni_3As_1 , Ni_3Fe_1 , Ni_3Cu_1 , Co_3Ge_1) with little or no available literature were predicted to be highly active for SMR based on DFT-calculated adsorption properties and MKM of SMR. This was the starting point of

Chapter 3, where an experimental study of some of the above-mentioned materials was conducted, serving as a validation of the model predictions.

Three bimetallic catalysts – $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$, $\text{Ni}_3\text{Fe}_1/\text{Al}_2\text{O}_3$, and $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ – were selected as they were promising candidates with relatively low toxicity and price. Alumina was selected as it is the most widely used commercial support material. The monometallic $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst was also included in the study to be used as the baseline scenario. A combined “experiment + simulation” approach was employed. The materials were synthesized and characterized, followed by SMR and SESMR testing in a lab-scale reactor. The numerical simulations were carried out in parallel with experimental testing, including DFT calculations of the carbon and oxygen adsorption energies on the bimetallic surfaces, and MKM of the SMR reaction. Based on the characterization of the materials, the addition of Cu improved the surface area and metal dispersion of the bimetallic $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ catalyst. These optimal characteristics were also reflected in its high SMR activity. Similarly, $\text{Ni}_3\text{Ge}_1/\text{Al}_2\text{O}_3$ showed a higher activity compared to the monometallic Ni catalyst. On the other hand, the addition of Fe was found to significantly decrease the activity of the bimetallic catalyst, which was also in contradiction with the conclusions obtained from previous literature [13], mentioned in Chapter 2. To understand this contradiction and also the reason why the three metals had different effects on Ni, an analysis of their carbon and oxygen adsorption energies was carried out. As metallic elements form crystallites with various surfaces (or facets) and different surfaces exhibit different adsorption abilities, it is important to identify the surfaces present in the samples synthesized. XRD analysis of the samples showed that (111) was the dominant surface with small amounts of (200) and (220) surfaces present, whereas in the literature [13] predictions were made based on the (211) surface. DFT calculations showed that there was in general a 0.5 – 1.0 eV difference between the adsorption energies on (111) and (211) surfaces, which was the origin of the different catalytic activity. Apart from the analysis of catalytic activity, the work also touched upon the stability of the catalysts, namely their coke resistance. TGA analysis showed that the addition of Cu, Fe, and Ge decreased the amount of coke deposited on the used catalysts, which was attributed to the formation of alloys and prevention of bulk Ni particle

formation. However, it should also be noted that this analysis was only based on rather short reaction times (~2 h), and the long-term stability of the materials remains to be investigated.

As $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ was identified as the optimal one among the three bimetallic catalysts, we took one step further in Chapter 4 to study the effect of Cu loading on the performance of the bimetallic catalysts. The same “experiment + simulation” approach as described in Chapter 3 was adopted. Three bimetallic Ni-Cu catalysts – $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ (high Ni loading), $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$ (medium Ni loading), and $\text{Ni}_1\text{Cu}_3/\text{Al}_2\text{O}_3$ (low Ni loading) – were synthesized and characterized, followed by SMR and SESMR testing. All three catalysts showed enhanced activity compared to $\text{Ni}/\text{Al}_2\text{O}_3$, but the effect was most significant for $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$. All catalysts exhibited a similar level of CO selectivity, the higher methane conversion of the bimetallic catalysts can therefore be interpreted by their tendency to convert methane into CO_2 , instead of CO. The promoting effect of Cu on the Ni catalyst is therefore attributed to its ability to enhance the WGS reaction, which takes place simultaneously with the SMR reaction. The high- and medium-loading Ni-Cu catalysts were then tested for SESMR using CaO as the CO_2 sorbent. Although the high-loading sample maintained the same level of methane conversion compared to $\text{Ni}/\text{Al}_2\text{O}_3$ with slightly higher hydrogen yield and purity, the medium-loading sample did not achieve similar results. This was possibly due to the lower reaction temperature (600 – 700 °C) of the SESMR process, as Cu is inactive at lower temperatures. Similar to Chapter 3, DFT calculations of the carbon and oxygen adsorptive energies on the (111) facet of the three Cu-loaded Ni surfaces were carried out. The adsorption ability of both high- and medium-loading surfaces was found to be very similar, which is consistent with the observations from the experimental tests. The low-loading surface showed a lower adsorptive ability towards the carbon atom, which is potentially the reason for its relatively low activity – the low concentration of Ni makes it difficult for the rate-determining methane decomposition step to take place. The amount of coke deposited on the used bimetallic catalysts was also analysed by TGA and it was concluded that a higher Cu loading is beneficial for the overall coke-resistant ability.

In Chapters 3 and 4, the catalytic activities of the bimetallic catalysts were thoroughly studied. Apart from its activity, one other important measurement of a good catalyst is its stability. The stability of a catalyst can include many aspects – robustness, tendency to sintering, and resistance to unwanted species in the reaction system (which is usually coke and sulphur in the case of SMR) [14]. Chapter 5 of this thesis is focused on the stability of bimetallic SMR catalysts. The sulphur resistance was chosen to be the subject of this study as poisoning by sulphur-containing species is one of the most important reasons for SMR catalyst deactivation [15]. Although some individual works have been carried out to investigate the performance of bimetallic catalysts in the presence of sulphur, there is a clear lack of studies to systematically evaluate the sulphur resistance of bimetallic materials. The aim of this study is therefore to identify highly active SMR catalysts with high sulphur resistance. The combination of DFT calculations and MKM has been proven to be an effective way to evaluate the activity of different materials. It was therefore adopted for the high throughput screening of bimetallic databases. As mentioned previously, the carbon and oxygen adsorption energies are needed in order to link a given material with the MKM-estimated catalytic activity. For a limited number of materials (such as in Chapters 3 and 4), these adsorption energies can be easily obtained with DFT calculations. However, as the number of materials increases, the computational burden can become too heavy and it can be unrealistic to obtain hundreds or thousands of data if we simply rely on DFT. This is the reason why ML was considered an alternative way to obtain large quantities of data with minimal computational time. Easily available elemental properties were used as input features, and a database containing DFT-calculated adsorption energies was used as the training dataset. By comparing the performance of different ML algorithms, the Ensemble Learning, ANN, and SVR models were proven to yield the best results with the highest R^2 value of 0.74. The ML model was then used to predict the carbon, oxygen, and sulphur adsorption energies on over 500 bimetallic surfaces. These materials were screened based on the carbon and oxygen adsorption energies, as well as the MKM previously developed in Chapter 3. Among the 500+ materials, 49 were listed as highly active catalysts for SMR. As the

adsorption energy prediction was based on the (111) facet, both Ni-Cu and Ni-Ge alloys were found to be on this list, which further confirmed the experimental findings in Chapters 3 and 4. The 49 materials were then filtered based on their sulphur adsorption energy and the ones with the weakest sulphur adsorptive ability were therefore identified as highly active sulphur-resistant SMR catalysts. The top ranked catalysts include Ni₃Cu₁, four Ge-based catalysts (Ge₃Cu₁, Ge₃Ni₁, Ge₃Co₁, Ge₃Fe₁), and three noble metal-based catalysts (Rh₃Co₁, Rh₃Fe₁, Ru₃Cu₁). This combined “ML + DFT + MKM” approach was concluded to be an effective method for the fast and accurate scanning of large material databases, which can be also applied to other chemical or pharmaceutical processes.

In summary, this PhD research successfully identified and evaluated the performance of novel bimetallic catalysts for the SMR and SESMR processes. Alumina-supported bimetallic Ni-Cu and Ni-Ge catalysts were found to be promising alternatives to conventional Ni-based materials. In particular, Ni-Cu catalysts achieved comparable catalytic activity as noble metal-based catalysts. It was also found that a maximum Cu concentration of 5 wt.% can be reached without negatively affecting the performance of the bimetallic catalysts. The application of these novel materials will enable the highly efficient production of hydrogen. Together with CaO as the CO₂ sorbent, the production of low-carbon high-purity hydrogen can be achieved. The relatively low Ni concentration in the catalysts is also favourable for the mass production of the materials, as Cu is more cost-effective and less toxic compared to Ni. On the other hand, the negative effect of Fe on Ni-based catalysts was explained by DFT-calculated adsorption energies and microkinetic modelling, proving the “DFT + MKM” approach to be an effective way of evaluating heterogeneous catalysis on an atomic scale. Further optimization of the “DFT + MKM” approach was achieved by combining it with ML, which allows for the rapid screening of large material databases. The data collected for the ML models in this work was also made available in an online repository, allowing for future uses by researchers working with any C-, O-, H-, and S-containing reactions. The work on sulphur-resistant catalysts from this PhD research also paves the way for future experimental

studies on the stability of novel bimetallic catalysts in the sulphur-existing SMR environment.

6.2 References

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7 Conclusions and future work

7.1 Conclusions

The use of hydrogen as a clean energy carrier is one of the most promising options for achieving the net zero goal. The most predominant hydrogen production pathway, SMR, can be improved to optimize its performance and decrease its negative environmental impact. This PhD research aims to investigate the catalytic activity and stability of novel bimetallic catalysts for both conventional SMR and the novel low-carbon high-purity hydrogen production technology, SESMR. In this section, the overall conclusions of this PhD thesis are presented with respect to the four objectives stated in Chapter 1.

1. Assess the performance of conventional SMR catalysts and identify potential bimetallic materials with high catalytic activity and stability under SMR conditions.

In Chapter 2, a literature review was carried out to understand and critically evaluate recent developments in using bi/polymetallic catalysts for (SE)SMR. The materials were evaluated based on three factors – physical-chemical properties, stability, and catalytic activity and selectivity. The catalysts mentioned in this chapter can be categorized into five main groups: noble metal-promoted Ni catalysts, non-noble metal-promoted Ni catalysts, metalloid-promoted Ni catalysts, Co-based catalysts, and other catalysts.

Noble metal-promoted Ni catalysts are generally considered the optimal choice for SMR due to their excellent performance. With less than 1 wt.% addition, the activity of the bimetallic catalysts can be largely enhanced, with methane conversion reaching or equalling the thermodynamic equilibrium level (~ 95%). The materials are also able to maintain high methane conversion for long-term SMR tests (> 24 h) due to the self-regeneration ability of the noble metals. It is also worth pointing out that the four commonly used noble metals (Ru, Rh, Pt, and Pd) are also able to self-activate, meaning that no or less than usual hydrogen is needed for the reduction of the catalysts.

Ni catalysts promoted by non-noble metals were also found to be promising candidates for SMR. While the addition of most non-noble elements (including Fe, Co, Cu) is able to enhance the long-term coke resistance of the bimetallic system, this was achieved at the expense of their catalytic activity. The promoting effect of metalloid elements was primarily evaluated using numerical simulations. By comparing DFT-calculated adsorption energies on the (211) surface of the bimetallic catalysts with results from a microkinetic model, Ge, As, and Sb were predicted to be promising candidates.

Apart from the type of promoters used, the structural design of the catalysts is also an important aspect to consider. Using a core-shell structure was found to be a good way to reduce the overall cost of the material, as the active metal(s) are mainly deposited on the outer layer of the support, and can therefore be utilized more efficiently.

2. Synthesize and characterize a conventional monometallic Ni/Al₂O₃ catalyst and three Ni-based bimetallic catalysts (Ni₃Cu₁/Al₂O₃, Ni₃Fe₁/Al₂O₃, and Ni₃Ge₁/Al₂O₃), and test their performance under SMR and SESMR conditions.

Taking into consideration the findings from the literature review, Ni-based catalysts promoted by Cu, Fe, and Ge were selected for further investigation. Chapter 3 presents the experimental and DFT study of the catalytic activity of the monometallic Ni/Al₂O₃ and bimetallic Ni₃Cu₁/Al₂O₃, Ni₃Fe₁/Al₂O₃, and Ni₃Ge₁/Al₂O₃ catalysts.

The methane conversion of Ni/Al₂O₃, Ni₃Cu₁/Al₂O₃, Ni₃Fe₁/Al₂O₃, and Ni₃Ge₁/Al₂O₃ at 800 °C was found to be 76%, 87%, 81%, and 40%, respectively. The promoting effect of Cu and Ge was attributed to their ability to enhance the WGS reaction, based on the CO selectivity values measured during the tests. The high activity of Ni₃Cu₁/Al₂O₃ was also attributed to its improved physical and chemical properties (e.g. higher surface area and metal dispersion) compared to the monometallic Ni catalyst. The addition of Fe was found to severely decrease the methane conversion of the bimetallic catalyst, although based on a previous study it was predicted to be highly active. The mismatch between the results was

explained by a combination of DFT calculations and MKM of the SMR reaction. The difference in atomic carbon and oxygen adsorption energies on different metal facets was found to be the source – the (111) facet, instead of (211), was predominant in the synthesized samples, and its adsorptive ability is unfavourable for the SMR reaction to take place. The amount of coke deposition was also evaluated for the used catalysts. All bimetallic catalysts showed a lower tendency for coke deposition, potentially due to the formation of alloy which prevents the formation of bulk Ni particles.

SESMR tests of the catalysts were also conducted, using CaO particles as the CO₂ sorbent. By continuously absorbing the CO₂ produced by the WGS reaction, the equilibrium of the overall reaction moves toward the direction of more hydrogen production. A ~20% increase was observed for methane conversion under the same temperature, with the highest conversion reaching 97% by Ni₃Cu₁/Al₂O₃ at 700 °C. Hydrogen yield and purity were also increased by 30% and 20%, respectively, with the highest values being 85% at 600 °C and 88% at 700 °C, both achieved by Ni₃Cu₁/Al₂O₃.

The bimetallic Ni-Cu catalyst is therefore considered to be a promising candidate to replace the conventional Ni-based materials, due to its enhanced activity and stability, as well as its lower price and toxicity. By applying Ni-Cu catalyst to the SESMR process, less energy requirement is needed to achieve a similar, or even better, level of performance compared to conventional SMR.

3. Investigate the effect of Cu loading on the performance of bimetallic Ni-Cu/Al₂O₃ catalysts for SMR and SESMR.

In Chapter 4, a further step was taken to investigate the influence of Cu loading on the performance of bimetallic Ni-Cu catalysts. Three different loading levels were considered, corresponding to low (Ni₃Cu₁/Al₂O₃), medium (Ni₁Cu₁/Al₂O₃), and high (Ni₁Cu₃/Al₂O₃) Cu loading, respectively. The addition of Cu in Ni catalysts is favourable due to its low cost and toxicity, as well as the low reduction temperature needed.

The methane conversion of $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$, $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$, and $\text{Ni}_1\text{Cu}_3/\text{Al}_2\text{O}_3$ at 800 °C was found to be 87%, 92%, and 77%, respectively, which are all higher than the methane conversion of 76% achieved by the monometallic Ni catalyst. This proved the excellent promoting effect of Cu, especially at higher SMR reaction temperatures. The enhanced catalytic activity of the bimetallic Ni-Cu catalysts was attributed to the enhancement of the WGS reaction, as well as the synergistic effect between Ni and Cu when a binary alloy is formed. Compared to $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$, the relatively lower activity of $\text{Ni}_1\text{Cu}_3/\text{Al}_2\text{O}_3$ was partly due to its high Cu loading (as Cu is less active for SMR), and partly due to the blocking of pores within the support by the large Ni_1Cu_3 crystallites. Similar to previously, CaO was then added to the system as the CO_2 sorbent. The highest methane conversion and hydrogen yield of 96% and 85% were achieved by $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ at 700 °C. However, the hydrogen purity level of 82% was inevitably lower than that at 600 °C, due to the exothermic nature of the CO_2 sorption process. The effect of Cu loading on the overall activity of the bimetallic catalysts was also explained by DFT calculations. The carbon and oxygen adsorption energies of $\text{Ni}_3\text{Cu}_1(111)$ and $\text{Ni}_1\text{Cu}_1(111)$ were found to be in the optimal range for SMR reaction to take place. Therefore, it can be concluded that a medium Cu loading is sufficient to achieve optimal performance for SMR, whereas a low Cu loading is necessary if the bimetallic catalyst is employed under SESMR conditions.

4. Screen bimetallic material databases for sulphur-resistant SMR catalysts, based on atomic adsorption energies predicted by ML models and results from DFT calculations and microkinetic modelling.

In Chapter 5, a combined “ML + DFT + MKM” approach was employed for the fast scanning of sulphur-resistant SMR catalysts. The carbon and oxygen adsorption energies calculated in previous chapters were used as part of the ML input database, combined with sulphur and hydrogen adsorption energies obtained from additional DFT calculations. The initial 21 input features were subjected to a feature importance evaluation and the elemental features of the adsorbates were found to be most relevant, including the enthalpy of fusion,

density, first ionization potential, and covalent radius. Ten different ML algorithms were tested and a hyperparameter tuning process was also carried out. With the tuned parameters, Support Vector Regression, Artificial Neural Network, and Ensemble learning were found to be the best-performing models. Although the Ensemble Learning model still shows some inaccuracies when predicting extreme values, it is able to capture the overall trend of the dataset with the highest R^2 value of 0.74. The model was then used to predict the carbon, oxygen, and sulphur adsorption energies of over 500 bimetallic alloys (focusing on the [111] facet). Based on the previously developed microkinetic model, we defined the region with a carbon adsorption energy of [-8.5, -7.0] eV and an oxygen adsorption energy of [6.5, -5.0] eV to be “highly active” for SMR. Of the 500+ candidates, 49 were identified to be in the “highly active” region. By further filtering the 49 candidates by their sulphur adsorption energy, the following were predicted to be potential sulphur-resistant SMR catalysts: Ge_3Cu_1 , Ge_3Ni_1 , Ge_3Co_1 , Ge_3Fe_1 , Rh_3Co_1 , Rh_3Fe_1 , Ru_3Cu_1 , and Ni_3Cu_1 .

Overall, this PhD successfully identified and tested novel bimetallic catalysts with enhanced activity and stability. The application of these promising materials will be able to aid in the production of clean hydrogen and the transition to a net zero future.

7.2 Recommendations for future work

In this section, the recommendations for future work are highlighted, which will hopefully advance the development of bimetallic SMR catalysts with optimal performance and provide inspiration for other areas of research in this similar field of study.

7.2.1 Long-term stability test

The catalytic activity of the bimetallic NiCu-, NiFe-, and NiGe-based catalysts has been thoroughly studied. However, more work is required to evaluate their stability. Although TGA analysis was carried out for the used catalysts, the reaction time of the tests involved in this work was rather short (~ 2 h). It is recommended that long-term SMR tests be conducted using the catalysts (> 24

h), followed by physisorption, SEM, and TGA analysis of the spent samples. Focus should be paid on the amount of coke deposited, the morphology of the coke and the spent catalysts, as well as the change in surface area and pore size distribution.

7.2.2 Optimization of the microkinetic model

The microkinetic model of the SMR reaction in this work was developed using a simplified version of the reaction mechanism. Although the current model provides sufficient accuracy, it is recommended that a model using a more refined reaction mechanism be developed for improved accuracy. It is also of interest to add the WGS reaction into the model as this reaction usually takes place simultaneously with SMR in reality.

7.2.3 Cyclic SESMR tests and alternative sorbents

As the SESMR process is not the main focus of this study, SESMR-related results presented in this thesis were obtained based on the pre-breakthrough period of non-cyclic tests, using untreated CaO as sorbent. In the future, it would be useful to test the bimetallic catalysts under cyclic SESMR conditions or combine them with other advanced sorbent materials for optimal results.

7.2.4 Improvement of machine learning models

Detailed suggestions for the improvement of the ML models were presented in section 5.3.3. In summary, the optimization of the ML models relies heavily on the size of the input database. Large DFT databases that are currently available online may not necessarily be readily usable – for example, an online database may only contain data for certain crystallite facet(s), which can be different from what is needed by the research. Also, data from different sources is usually calculated with different parameters or methods, which may pose difficulty when combining data from several sources as the input database for the ML model. It is therefore recommended that DFT calculations be carried out for the atomic adsorption energies of H, S, N, and potentially Cl on commonly seen surfaces (e.g. (111), (200), and (220)).

7.2.5 Experimental testing of materials with predicted high sulphur resistance

In this work, several bimetallic materials were predicted to be active SMR catalysts with high sulphur resistance. Amongst the 8 materials, only Ni_3Cu_1 has been tested for its catalytic activity, while the sulphur resistance of all materials remains unknown. A recommended next step for this study is to test these materials under SMR conditions in the presence of commonly seen sulphur-containing species (e.g. 20 – 100 ppm of H_2S), to simulate the sulphur-containing natural gas streams that are usually used for industrial SMR processes.

7.2.6 Other roles for the combined “ML + DFT + MKM” approach

The combined “ML + DFT + MKM” approach, which applies Machine Learning-predicted DFT data to a microkinetic model, has been proven to be highly efficient for the screening of large material databases. By adjusting the input database and features for the ML model and by replacing the MKM of SMR with other target reactions, this approach can be applied to the fast scanning of any materials of interest.

7.2.7 Techno-economic analysis of the application of the bimetallic catalysts

The addition of Cu and Ge to the conventional Ni-based catalysts has been demonstrated to enhance catalytic activity, particularly with bimetallic Ni-Cu catalysts being highly promising. It is therefore of interest to carry out a comprehensive techno-economic analysis of these catalysts, including their fabrication, pretreatment, application, and potential disposal processes. Comparisons with conventional Ni-based catalysts will provide valuable insights into the potential of Ni-Cu-based catalysts for large-scale applications.

Appendices

Appendix A Ethical approval letter



5 May 2021

Dear Ms Wang ,

Reference: CURES/13122/2021

Title: Designing new bi/tri-metallic catalysts with enhanced catalytic activity for SESMR using the QSPR/QSAR method

Thank you for your application to the Cranfield University Research Ethics System (CURES).

We are pleased to inform you your CURES application, reference CURES/13122/2021 has been reviewed. You may now proceed with the research activities you have sought approval for.

If you have any queries, please contact CURES Support.

We wish you every success with your project.

Regards,

CURES Team

Figure A-1 Ethical approval letter for this PhD work.

Appendix B Supplementary information for Chapter 3

B.1 Setup of the fixed bed reactor system

The setup of the fixed bed reactor system used to carry out all SMR and SESMR tests in this work is presented in Figure B-1.

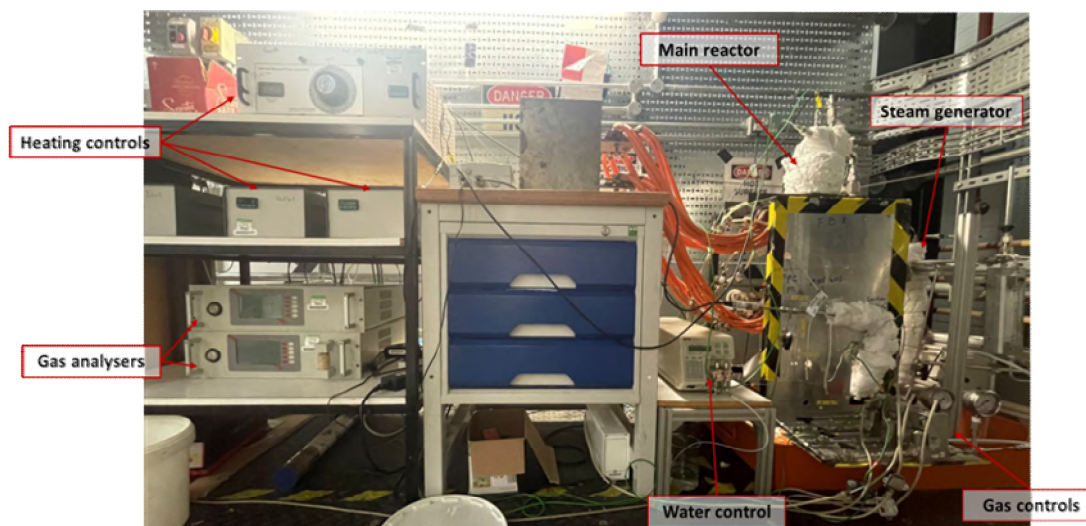
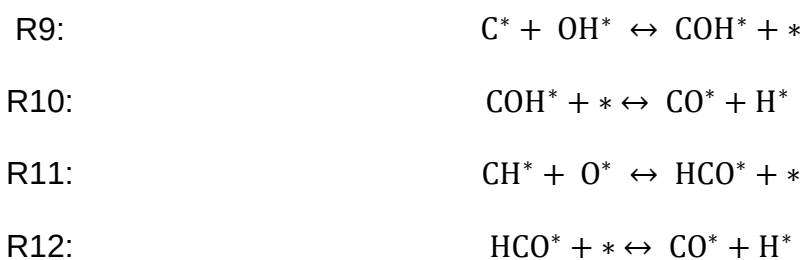


Figure B-1 Setup of the fixed bed reactor system.

B.2 Elementary steps of the steam methane reforming reaction

The elementary reaction steps involved in the SMR reaction were defined based on previous literature on the microkinetic modelling of steam reforming and studies on the reaction mechanism of SMR [1–4]. The reaction steps are listed below, where * denotes a vacant adsorption site, and $C_xH_yO_z^*$ denotes the adsorbed species.





B.3 Adsorption energies obtained using DFT and the UBI-QEP method

In this work, the energies of all gas phase species and the adsorption energies of C, H, and O on the metal surfaces were calculated using DFT. The computational details are described in the methodology section. The adsorption energies of the $C_xH_yO_z$ were obtained using the improved UBI-QEP method described in the work by Wang et al. [1]. A summary of the adsorption energies involved in the reaction model is presented in Table B-1.

Table B-1 Summary of the adsorption energies involved in the reaction.

	Total energy of gas phase species (eV)	Adsorption energy (eV)						
		Ni[111]	Cu[111]	Fe[110]	Pd[111]	Au[111]	Pt[111]	Rh[111]
C	-241.8	-7.86	-6.35	-8.52	-7.92	-5.56	-8.21	-8.36
H	-12.5	-3.10	-3.06	-4.21	-3.00	-2.61	-3.18	-2.17
O	-558.3	-5.36	-4.70	-6.47	-4.43	-3.09	-4.43	-4.93
CH ₄	-315.5	-0.65	-0.08	-0.22	-0.17	-0.65	-0.19	-0.20
CH ₃	-296.6	-1.93	-1.50	-2.13	-1.95	-1.29	-2.03	-2.08
CH ₂	-277.9	-3.76	-2.70	-4.24	-3.80	-2.19	-4.01	-4.12
CH	-259.8	-5.23	-3.92	-5.82	-5.29	-3.25	-5.54	-5.68
H ₂ O	-597.4	-0.37	-0.75	-1.26	-0.68	-0.36	-0.68	-0.81
OH	-577.6	-2.86	-2.35	-3.75	-2.15	-1.23	-2.15	-2.53
CO	-814.4	-1.16	-1.16	-2.02	-1.76	-0.90	-1.88	-1.95
HCO	-828.8	-3.04	-2.15	-3.46	-3.08	-1.72	-3.26	-3.36

COH	-826.9	-4.45	-3.26	-4.99	-4.50	-2.67	-4.73	-4.86
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B.4 Generalized formation energies

The energies in the CatMAP software are computed as “relative free energies of formation” relative to a set of common reference [5]. In this study, C in CH₄, H in H₂, and O in H₂O were selected as the reference. The equations for calculating the reference energies are listed below:

$$\text{Carbon (C):} \quad R_C = U_{\text{CH}_4} - 4U_H$$

$$\text{Hydrogen (H):} \quad R_H = 0.5U_H$$

$$\text{Oxygen (O):} \quad R_O = U_{\text{H}_2\text{O}} - 2U_H$$

$$\text{Gas phase species:} \quad E_{\text{C}_x\text{H}_y\text{O}_z} = U_{\text{C}_x\text{H}_y\text{O}_z} - xR_C - yR_H - zR_O$$

$$\text{Adsorbed species:} \quad E_{\text{C}_x\text{H}_y\text{O}_z^*} = U_{\text{C}_x\text{H}_y\text{O}_z^*} - U_{\text{slab}} - xR_C - yR_H - zR_O$$

Where R_i is the reference energy, U_i is the DFT-calculated total energy, and E the generalized formation energy which is used in the input file for the microkinetic model. Table B-2 summarises the generalized formation energies of all species involved in the microkinetic model.

Table B-2 Summary of the generalized formation energies used in the microkinetic model.

	Ni[111]	Cu[111]	Fe[110]	Pd[111]	Au[111]	Pt[111]	Rh[111]
C	2.55	4.06	1.89	2.49	4.85	2.20	2.05
H	0.15	0.19	-0.96	0.25	0.64	0.07	1.08
O	2.19	2.85	1.08	3.12	4.46	3.12	2.62
CH ₄	-0.65	-0.08	-0.22	-0.17	-0.65	-0.19	-0.20
CH ₃	1.15	1.58	0.95	1.13	1.79	1.05	1.00
CH ₂	2.21	3.27	1.73	2.17	3.78	1.96	1.84
CH	3.03	4.35	2.44	2.98	5.01	2.72	2.58
H ₂ O	-0.37	-0.75	-1.26	-0.68	-0.36	-0.68	-0.81
OH	1.10	1.60	0.21	1.81	2.73	1.81	1.43

CO	2.55	2.55	1.69	1.95	2.81	1.82	1.76
HCO	2.00	2.90	1.58	1.96	3.33	1.78	1.69
COH	2.51	3.70	1.97	2.46	4.29	2.23	2.10

B.5 Estimation of activation energies using the BEP relationship

In this study, the activation energies of the reactions were estimated using the BEP approach, which greatly lessened the computational burden. The BEP relationship states that the activation barrier of a given reaction (E_a) is proportionally linked to the enthalpy of the reaction (ΔH), as shown in the equation below:

$$E_a = \alpha \cdot \Delta H + \beta$$

The classification of each reaction and the corresponding parameters used for the BEP relationship are summarised in Table B-3. The parameters were extracted from the work by Wang et al. [1].

Table B-3 Classification and parameters of the BEP relationship for the reactions involved in the model.

Reaction	Classification	BEP parameters (α , β)
R1	C-H bond cleavage in C_xH_y fragment	0.89, 0.75
R2	C-H bond cleavage in C_xH_y fragment	0.89, 0.75
R3	C-H bond cleavage in C_xH_y fragment	0.89, 0.75
R4	C-H bond cleavage in C_xH_y fragment	0.89, 0.75
R5	O-H bond cleavage	0.11, 0.98
R6	O-H bond cleavage	0.11, 0.98
R7	C-O bond combination	0.69, 1.99
R8	H-H bond combination	0.02, 0.91
R9	C-O bond combination	0.69, 1.99

R10	O-H bond cleavage	0.11, 0.98
R11	C-O bond combination	0.69, 1.99
R12	C-H bond cleavage in H ₂ CO fragment	0.89, 0.75

B.6 Microkinetic model

The microkinetic model is developed using the CatMAP software, which generates the reaction rate of a given system by solving a mean-field model to the steady state. The generalized formation energies in Table B-2 and the BEP estimated activation energies using the parameters in Table B-3 are used as the input data for the microkinetic model. The Shomate equation was used for gas thermochemistry approximations, with parameters extracted from the National Institute of Standards and Technology (NIST) database [6]. The frozen adsorbate option was chosen for adsorbate thermochemistry, which assumes no free energy contribution from the adsorbates. The reaction conditions were set to be $T = 800\text{ }^{\circ}\text{C}$, $P = 1\text{ bar}$, with gas phase composition of 40% CH₄, 40% H₂O, 5% CO, and 15% H₂.

B.7 References

- [1] Wang Y, Xiao L, Qi Y, Mahmoodinia M, Feng X, Yang J, et al. Towards rational catalyst design: Boosting the rapid prediction of transition-metal activity by improved scaling relations. *Physical Chemistry Chemical Physics* 2019;21:19269–80. <https://doi.org/10.1039/c9cp04286e>.
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- [3] Xu Y, Lausche AC, Wang S, Khan TS, Abild-Pedersen F, Studt F, et al. In silico search for novel methane steam reforming catalysts. *New J Phys* 2013;15. <https://doi.org/10.1088/1367-2630/15/12/125021>.

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- [5] Medford AJ, Shi C, Hoffmann MJ, Lausche AC, Fitzgibbon SR, Bligaard T, et al. CatMAP: A Software Package for Descriptor-Based Microkinetic Mapping of Catalytic Trends. *Catal Letters* 2015;145:794–807. <https://doi.org/10.1007/s10562-015-1495-6>.
- [6] U.S. Department of Commerce. National Institute of Standards and Technology n.d. <https://www.nist.gov/> (accessed October 24, 2023).

Appendix C Supplementary information for Chapter 4

C.1 Physisorption isotherms

The isotherms of the calcined and reduced samples are presented in the following figures.

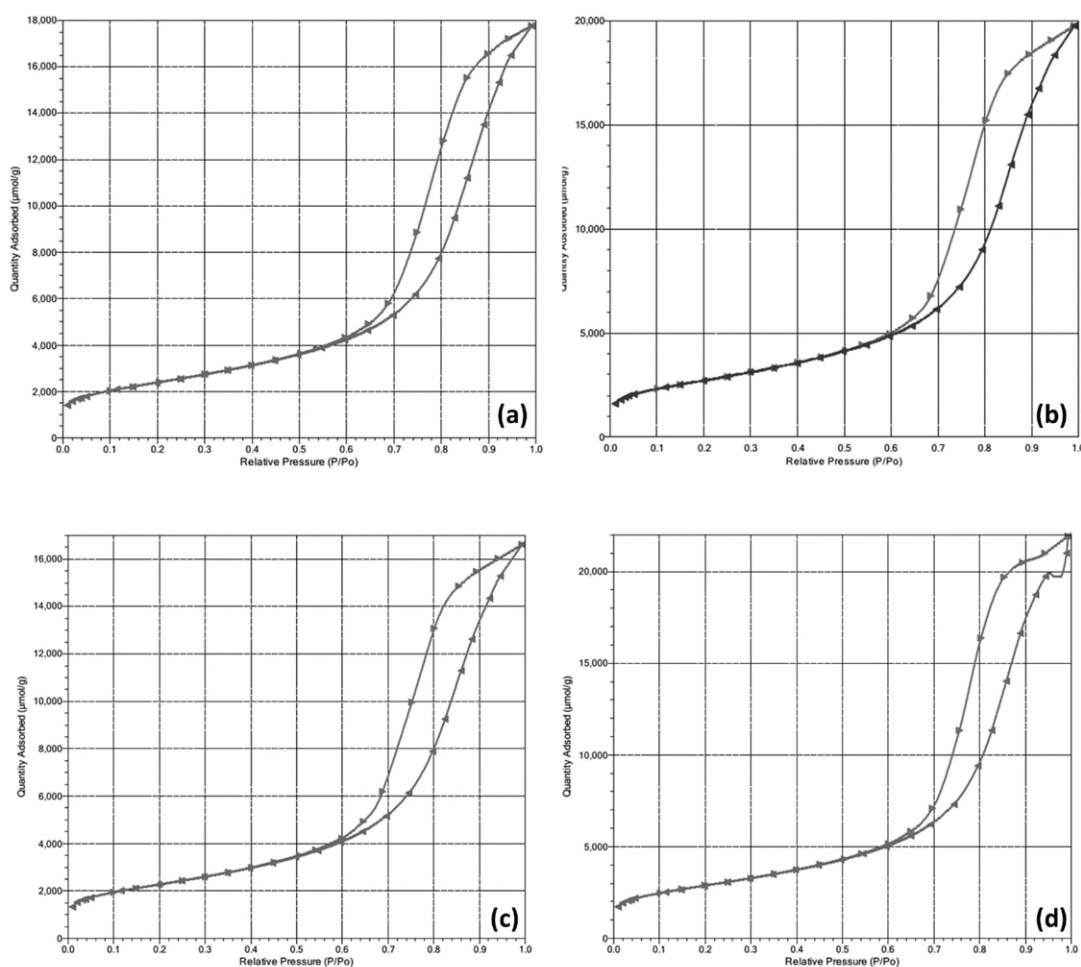


Figure C-1 Isotherms of the calcined samples: (a) $\text{Ni}/\text{Al}_2\text{O}_3$ (b) $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ (c) $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$ (d) $\text{Ni}_1\text{Cu}_3/\text{Al}_2\text{O}_3$. (Curves with arrows pointing upwards indicate the adsorption process and curves with arrows pointing downwards indicate the desorption process.)

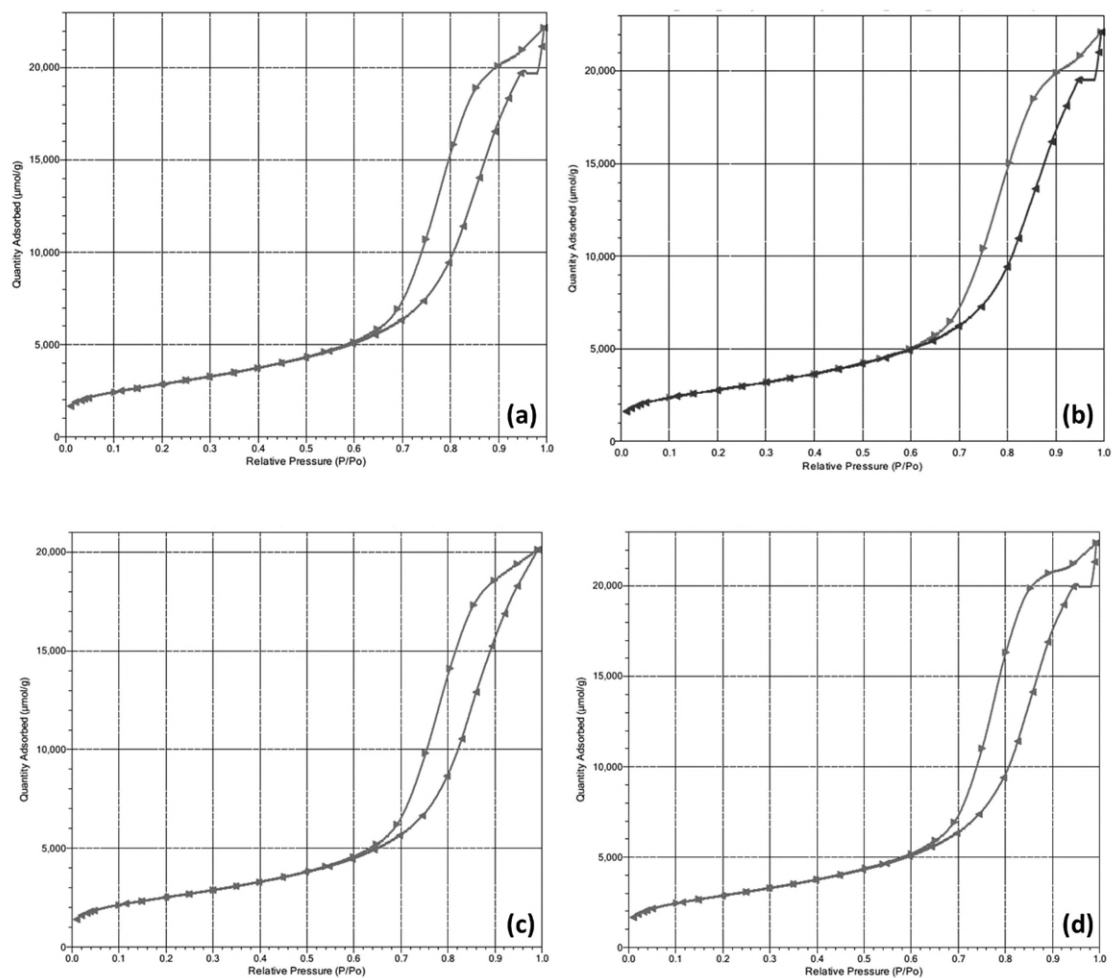


Figure C-2 Isotherms of the reduced samples: (a) $\text{Ni}/\text{Al}_2\text{O}_3$ (b) $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ (c) $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$ (d) $\text{Ni}_1\text{Cu}_3/\text{Al}_2\text{O}_3$. (Curves with arrows pointing upwards indicate the adsorption process and curves with arrows pointing downwards indicate the desorption process.)

Appendix D Supplementary information for Chapter 5

D.1 Input dataset for Machine Learning model development

The 12 features used to describe the metallic elements are group, period, atomic number, atomic mass, covalent radius, Pauling electronegativity, enthalpy of fusion, density, first ionization potential, surface free energy, work function, and Wigner Seitz radius. The 9 features used to describe the adsorbates are group, period, atomic number, atomic mass, covalent radius, Pauling electronegativity, enthalpy of fusion, density, and first ionization potential.

The numerical values of the features and adsorption energies used as the input dataset for the ML model training process can be found online from the Cranfield Online Research Data (CORD) repository at <https://doi.org/10.17862/cranfield.rd.24512788.v1>.

D.2 Input dataset for Microkinetic Model development

All information on the dataset and conditions used for the Microkinetic Model can be found in Appendix B.

D.3 Predicted adsorption energies

The C, H, O, and S adsorption energies on the 500+ bimetallic surfaces predicted by the ML model can be accessed online from the CORD repository at <https://doi.org/10.17862/cranfield.rd.24486466>.

D.4 Promising catalysts identified by the screening process

The promising candidates for the SMR reaction identified by the Microkinetic Model are listed in Table B-4.

Table B-4 Catalysts with optimal performance identified through the screening process.

Bimetallic catalyst with a M1:M2 molar ratio of 3:1			Adsorption energy (eV)		
No.	M1	M2	C	O	S
1	Ge	Cu	-7.62650	-5.01768	-5.02157
2	Ge	Ni	-7.67237	-5.08801	-5.12017
3	Rh	Co	-7.30665	-5.14343	-5.18526
4	Rh	Fe	-7.17542	-5.16505	-5.30687
5	Ge	Co	-7.50246	-5.17161	-5.33429
6	Ni	Cu	-7.67273	-5.10829	-5.43571
7	Ge	Pd	-8.16988	-5.00004	-5.44785
8	Ge	Fe	-7.34338	-5.15616	-5.45589
9	Tc	Ni	-8.17942	-5.05062	-5.50654
10	Ru	Cu	-8.03899	-5.10794	-5.59828
11	Co	Cu	-7.67982	-5.19725	-5.68112
12	Ru	Ni	-8.11078	-5.22111	-5.69688
13	Tc	Co	-8.16705	-5.21196	-5.72066
14	Ni	Co	-7.57855	-5.3748	-5.74842
15	Co	Ni	-7.70955	-5.27347	-5.77972
16	Ge	Rh	-7.94664	-5.1144	-5.79988
17	Tc	Fe	-8.09804	-5.23099	-5.84227
18	Zn	Rh	-7.04996	-5.0047	-5.8551

19	Ni	Pd	-8.40054	-5.11331	-5.86198
20	Mo	Co	-8.48787	-5.11887	-5.86362
21	Ni	Fe	-7.44876	-5.40117	-5.87003
22	Fe	Cu	-7.98197	-5.24044	-5.90131
23	Ru	Co	-8.06237	-5.39127	-5.911
24	Cu	Rh	-7.42594	-5.12412	-5.91599
25	Mo	Fe	-8.42501	-5.12581	-5.98522
26	Pd	Ru	-7.21282	-5.26812	-5.9991
27	Fe	Ni	-7.99754	-5.3142	-5.99991
28	Ru	Fe	-7.95624	-5.40468	-6.0326
29	Co	Pd	-8.45703	-5.19666	-6.1074
30	Co	Fe	-7.53317	-5.51052	-6.11544
31	Rh	Tc	-7.26201	-5.06673	-6.20417
32	Ni	Rh	-8.11137	-5.29894	-6.21402
33	Fe	Co	-7.95683	-5.52296	-6.21403
34	Rh	Ru	-7.67187	-5.50068	-6.23871
35	Ge	Tc	-7.22822	-5.03607	-6.35319
36	Ge	Ru	-7.48506	-5.29524	-6.38774
37	Co	Rh	-8.18295	-5.39004	-6.45943
38	Cu	Ru	-7.01998	-5.48503	-6.50385
39	Fe	Rh	-8.45292	-5.4239	-6.67963
40	Ni	Tc	-7.30862	-5.2763	-6.76733

41	Tc	Ru	-8.47608	-5.56946	-6.77411
42	Ni	Ru	-7.58614	-5.64244	-6.80187
43	Ru	Tc	-7.96193	-5.4105	-6.9299
44	Co	Tc	-7.45794	-5.37037	-7.01274
45	Co	Ru	-7.69492	-5.74318	-7.04729
46	Ru	Mo	-7.47125	-5.13888	-7.21184
47	Fe	Tc	-7.80207	-5.40444	-7.23293
48	Fe	Ru	-7.96675	-5.76451	-7.26748
49	Fe	Mo	-7.17289	-5.06135	-7.51487

D.5 References

- [1] Wang Y, Xiao L, Qi Y, Mahmoodinia M, Feng X, Yang J, et al. Towards rational catalyst design: Boosting the rapid prediction of transition-metal activity by improved scaling relations. *Physical Chemistry Chemical Physics* 2019;21:19269–80. <https://doi.org/10.1039/c9cp04286e>.
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