

Full Length Article

Experimental and DFT study of (sorption-enhanced) steam methane reforming over bimetallic Ni-Cu catalysts

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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 (800 °C), 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.

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 the 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. [8–10] 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 produc-

Abbreviations: At.%, Atomic percentage; BET, Brunauer–Emmett–Teller; BJH, Barrett–Joyner–Halenda; DFT, Density Functional Theory; GHSV, Gas hourly space velocity; ICDD, The International Centre for Diffraction Data; MKM, Microkinetic Model; Mol.%, Molar percentage; PAW, Projector augmented wave; EDX, Energy dispersive X-ray analysis; SEM, Scanning electron microscopy; SMR, Steam methane reforming; SESMR, Sorption-enhanced steam methane reforming; vol.%, Volume percentage; XRF, X-ray fluorescence analysis; wt.%, Weight percentage; WGS, Water-gas shift.

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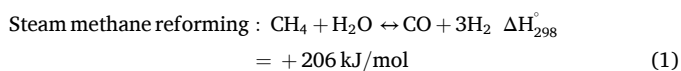
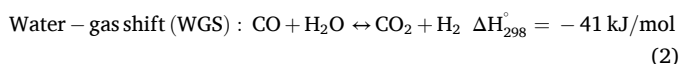
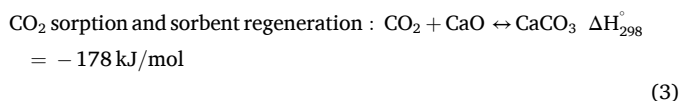
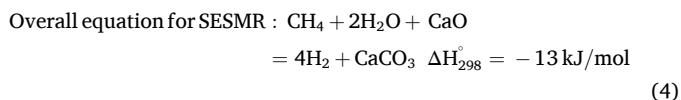
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tion of high-purity hydrogen with simultaneous *in-situ* carbon capture using a CO₂ sorbent (e.g. CaO). The equations of all reactions taking place in both SMR and SESMR are listed below.



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.

2. Experimental

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). 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 h. 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.

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 μA, with quantification calculated using the “Fundamental Parameters” approach. The samples were reduced in a 10 vol.% hydrogen flow (balanced by nitrogen) prior to the XRF analysis. To ensure that the final result is representative, three batches of samples were selected randomly for each catalyst, and the averaged results are presented in this paper.

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

working distance of 10 mm and a voltage of 20 kV.

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 a 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 Kα radiation. The reduced samples were crushed into a powder and scanned in the 2θ 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 Kα 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.

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 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:

$$\text{carbon amount (wt.\%)} = \frac{\text{weight of carbon deposited on the sample}}{\text{weight of sample used for TGA}} \quad (5)$$

2.3. Evaluation of catalytic activity

A fixed bed reactor described in the work by Shen et al. [13,14 14] 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 SMR tests under the three different temperatures were carried out consecutively. After the test at T = 600 °C was completed, both steam and methane flows were stopped, the system was purged by a nitrogen flow of 20 ml/min and the temperature was raised to 700 °C. Then, steam was introduced to the system (with the desired flow rate) without the methane flow for at least 10 min. The purpose of this step is to eliminate any potential influence on the following tests due to carbon deposited on the catalyst surface during the previous test. After the outlet gas composition was stabilized, methane was introduced to the system to initiate the SMR reaction. The same procedure was repeated after the T = 700 °C test was completed.

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 (balanced with nitrogen) at 850 °C for the reduction of the active metals and the calcination of the sorbent. A figure of the experimental setup can be found in [Supplementary Information](#).

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 above-mentioned parameters for the SESMR tests were calculated based on the pre-breakthrough stage, which lasted for approximately 10 min for each test. The equations used for calculating these parameters are listed below:

$$\text{CH}_4 \text{ conversion} = \frac{\dot{n}(\text{CH}_4 \text{ in}) - \dot{n}(\text{CH}_4 \text{ out})}{\dot{n}(\text{CH}_4 \text{ in})} \quad (6)$$

$$\text{H}_2 \text{ yield} = \frac{\dot{n}(\text{H}_2 \text{ out})}{4 \times \dot{n}(\text{CH}_4 \text{ in})} \quad (7)$$

$$\text{H}_2 \text{ purity} = \frac{\dot{n}(\text{H}_2 \text{ out})}{\dot{n}(\text{CH}_4 \text{ out}) + \dot{n}(\text{H}_2 \text{ out}) + \dot{n}(\text{CO out}) + \dot{n}(\text{CO}_2 \text{ out})} \quad (8)$$

$$\text{CO selectivity} = \frac{\dot{n}(\text{CO out})}{\dot{n}(\text{CO out}) + \dot{n}(\text{CO}_2 \text{ out})} \quad (9)$$

where $\dot{n}(iin)$ and $\dot{n}(iout)$ are the molar flow rate of the gas i when entering and exiting the reaction system. The concentrations of the gases were monitored and recorded by a continuous multi-gas analyser (which measures the concentration of CH₄, H₂, CO, and CO₂ in vol.%), and a Vaisala HMT330 humidity probe (which measures the concentration of H₂O). Considering that the reaction temperature was high, the gases can be assumed to be ideal gases. The molar flow rate of each can therefore be obtained based on the total flow rate and the volumetric concentration. Although the total molar number of the gases exiting the reaction system can change depending on the extent of each reaction (Equations (1) and (2)) [15], this does not affect the accuracy of the final results as

the calculations were performed on a concentration basis.

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 [16]. The ionic cores were described by the projector augmented wave (PAW) method [17]. The generalized gradient approximation (GGA) functional with the Perdew-Burke-Ernzerhoff (PBE) functional was used to describe the exchange correlation [18]. 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:

$$E_{\text{ads}} = E_{\text{adsorbate+slab}} - E_{\text{adsorbate}} - E_{\text{slab}} \quad (10)$$

Where $E_{\text{adsorbate+slab}}$, $E_{\text{adsorbate}}$ and E_{slab} are the total energies of the surface with the adsorbed molecule, the molecule in gas-phase and the clean slab, respectively. Brillouin zone sampling of the surface slabs was performed using a 3 × 3 × 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 definition of each site are illustrated in [Fig. 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.

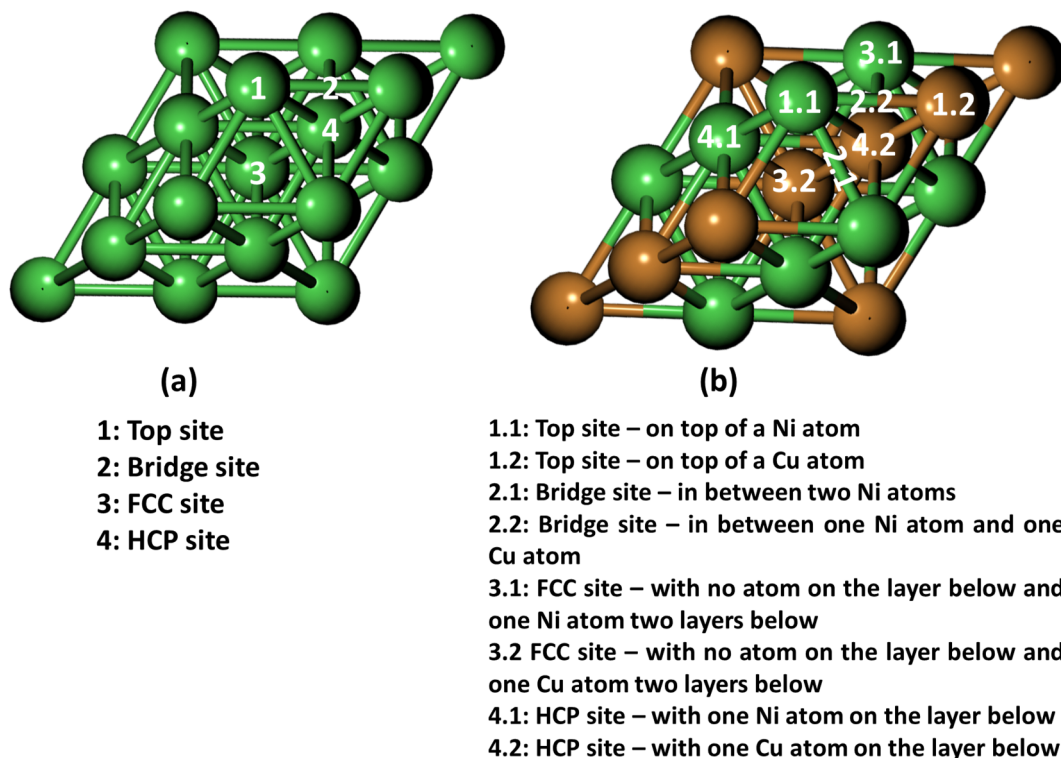


Fig. 1. Illustration of the adsorption sites on the (a) monometallic surfaces and (b) bimetallic surfaces. (Green atoms: Ni, brown atoms: Cu.).

2.5. Microkinetic modelling

The microkinetic model of the SMR reaction was developed using the CatMAP Python module [19]. 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 Fig. 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].

3. Results and discussion

3.1. Characterization

3.1.1. XRF analysis

Results from the XRF analysis are summarized in Table 1. Although the total metal loading of Ni/Al₂O₃, Ni₁Cu₁/Al₂O₃, and Ni₁Cu₃/Al₂O₃ 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.

3.1.2. SEM-EDX analysis

The SEM images of the synthesized materials are presented in Fig. 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. Fig. 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 Fig. 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 was obtained by EDX analysis and the elemental mappings are presented in Fig. 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.

3.1.3. Physisorption

The results obtained from the N₂ physisorption analysis are summarised in Table 2, the isotherms obtained from the tests are available in Supplementary Information. The isotherms are consistent with type IV

Table 1

Theoretical and measured total metal loading and Ni:Cu molar ratio.

	Total metal loading (wt.%)		Ni:Cu molar ratio	
	Theoretical	Measured	Theoretical	Measured
Ni/Al ₂ O ₃	10	9.5	–	–
Ni ₃ Cu ₁ /Al ₂ 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	1: 3	1.0: 2.9

mesoporous materials with the type H₃ hysteresis loop, indicating the potential formation of parallel plate-shaped pores [20]. 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 [21,22]. 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 [23], 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 [24].

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 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 to H₂ adsorption compared to Ni [25]. 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.

3.1.5. XRD analysis

The XRD patterns of the bare alumina support and the reduced bimetallic catalysts are presented in Fig. 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 Fig. 5 (a) correspond to the (111), (200), and (220) phase 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 [26], as shown in Fig. 5 (b). The four dotted lines shown in Fig. 5 (b) represent the 2θ angles of 43.2°, 44.5°, 50.5°, and 51.9°, which correspond to the Cu(111) (ICDD File #003–1018), Ni(111) (ICDD File #004–0850), Cu(200) (ICDD File #003–1018), and Ni(200) (ICDD File #004–0850) phases, respectively. 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 [27].

3.1.6. XPS analysis

The XPS profiles of the reduced monometallic Ni/Al₂O₃ and bimetallic Ni-Cu catalysts are presented in Fig. 6. Two main peaks centred at approximately 856.2 and 873.5 eV are observed in the Ni 2p spectra (Fig. 6 (a)), which correspond to the 2p 3/2 and 2p 1/2 peak of Ni²⁺ (NiO) with strong interaction with the alumina support [28,29]. Two

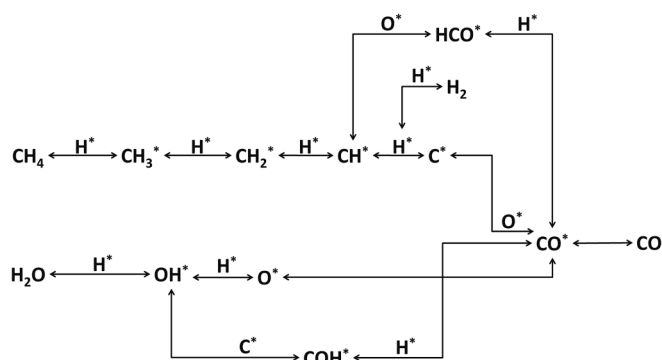


Fig. 2. Reaction pathway of the SMR reaction.

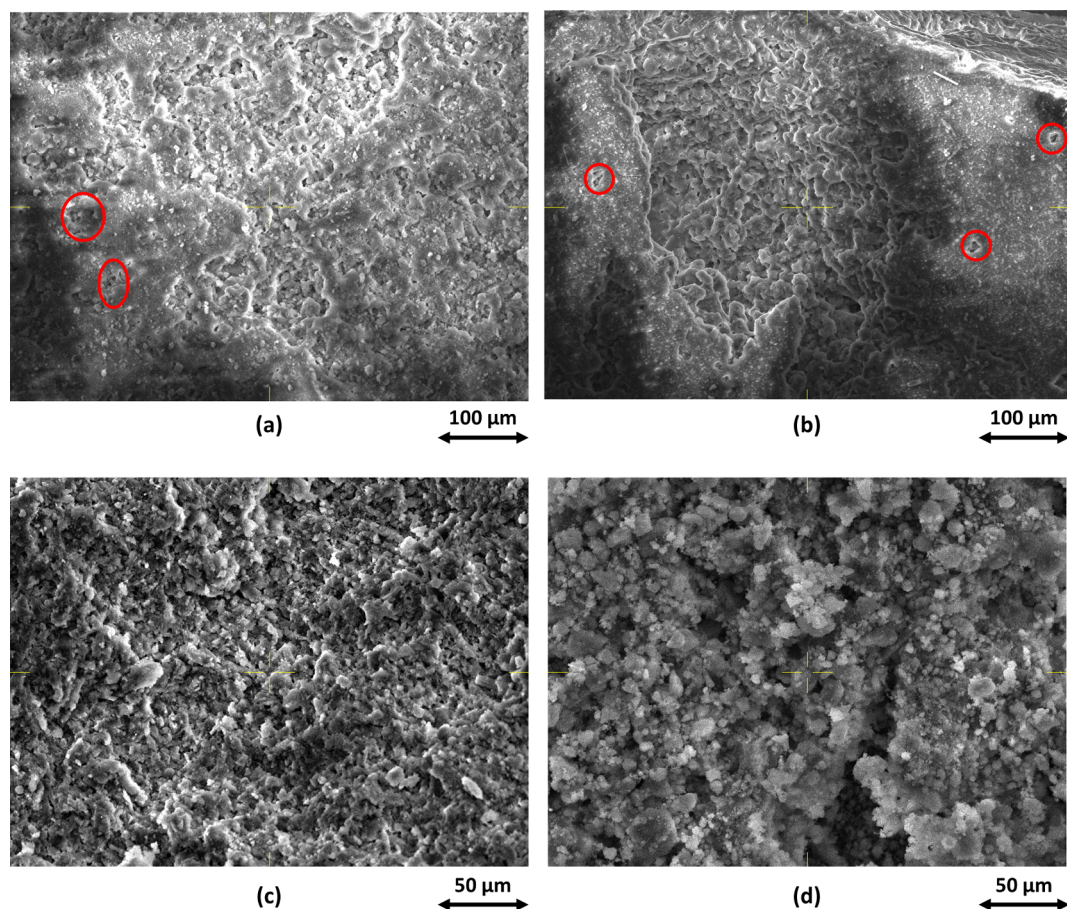


Fig. 3. SEM images of the outer layer of the (a) Ni/Al₂O₃ and (b) Ni₁Cu₁/Al₂O₃ pellets, and the particles of (c) Ni/Al₂O₃ and (d) Ni₁Cu₁/Al₂O₃.

satellite peaks with lower intensity were observed at the higher binding energy side of the main peaks, which is a typical characteristic of NiO [30]. An additional peak at approximately 853 eV was observed for Ni/Al₂O₃, corresponding to the metallic Ni⁰. In the Cu 2p spectra (Fig. 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 [28]. 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.

3.2. Catalytic performance study for steam methane reforming

The catalytic performance of the catalysts was evaluated based on CH₄ conversion (Equation (6)), H₂ yield (Equation (7)) and purity (Equation (8)), and CO selectivity (Equation (9)). 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 Fig. 7.

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 Fig. 7 (d), all catalysts showed a similar level of CO selectivity at 800 °C. However, CH₄ conversion of the bimetallic catalysts is shown to be higher than Ni/Al₂O₃ (Fig. 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. Considering that the duration of the test at a fixed temperature is relatively short (less than 30 min), the change in catalyst weight due to carbon deposition may be too small to be accurately measured and calculated by TGA. The carbon amounts presented in Table 4 are therefore the accumulative amount of carbon deposited on the catalyst surfaces as reaction temperature increased from 600 to 800 °C. However, as described in the methodology section, each time after the reaction temperature was raised to the desired temperature, steam was introduced to the system (without methane) until the outlet gas composition was stable. For all tests, no significant change in the outlet

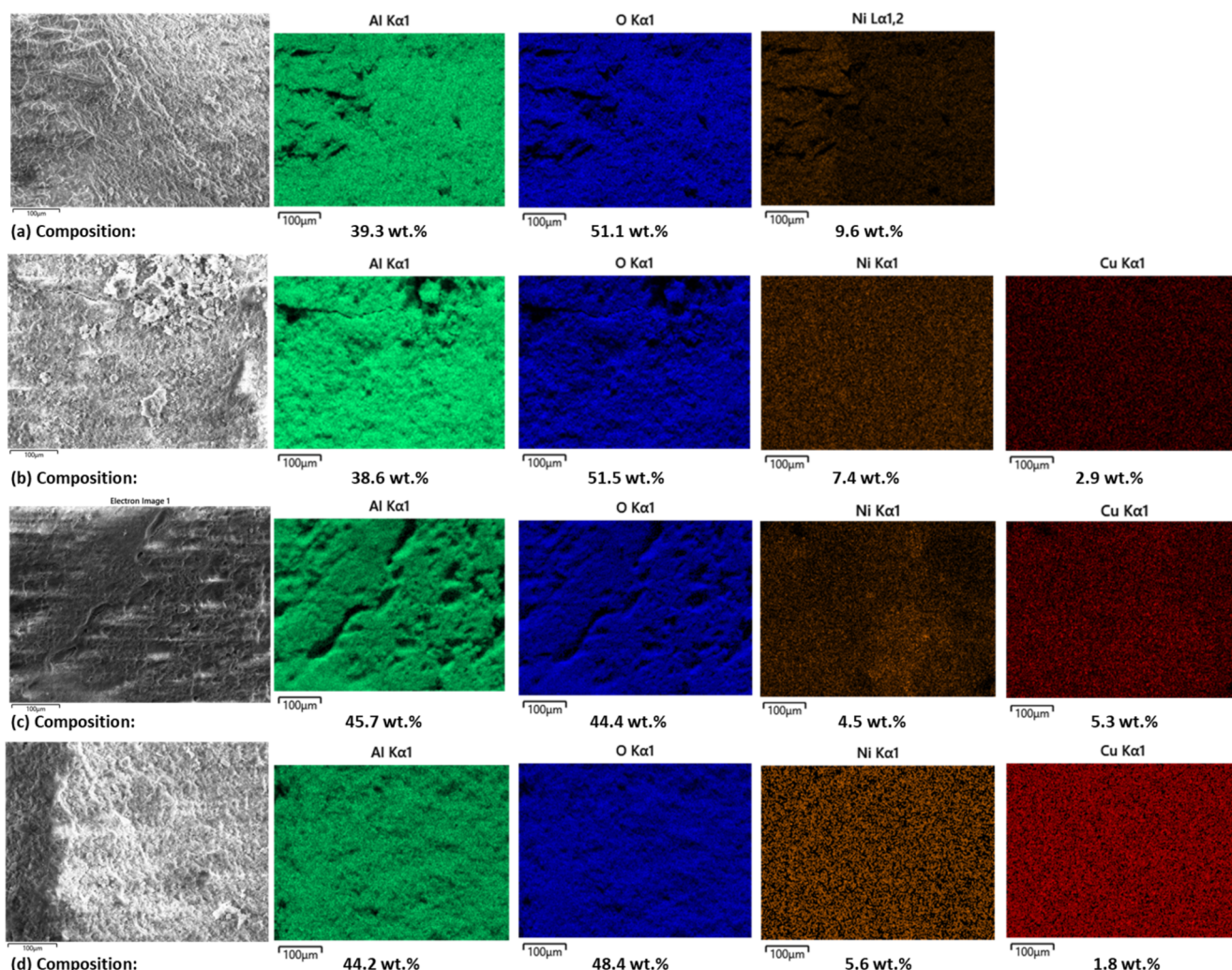


Fig. 4. EDX elemental mapping of (a) Ni/Al₂O₃, (b) Ni₃Cu₁/Al₂O₃, (c) Ni₁Cu₁/Al₂O₃, (d) Ni₁Cu₃/Al₂O₃.

Table 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)	
	Fresh	Reduced	Fresh	Reduced	Fresh	Reduced
Alumina	227.2		0.77		12.22	
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

gas composition was observed. Therefore, any potential influence due to previously deposited carbon was eliminated before the actual SMR reaction commenced.

Compared with the reduced catalysts, the used catalysts showed 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. [31], where the addition of 2.5 – 5 wt% Cu largely

Table 3

Results from H₂ pulse chemisorption analysis.

	H ₂ uptake (μmol/g)	Metal dispersion (%)	Metallic surface area		Crystallite size (Å)
			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

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 [31]. 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 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

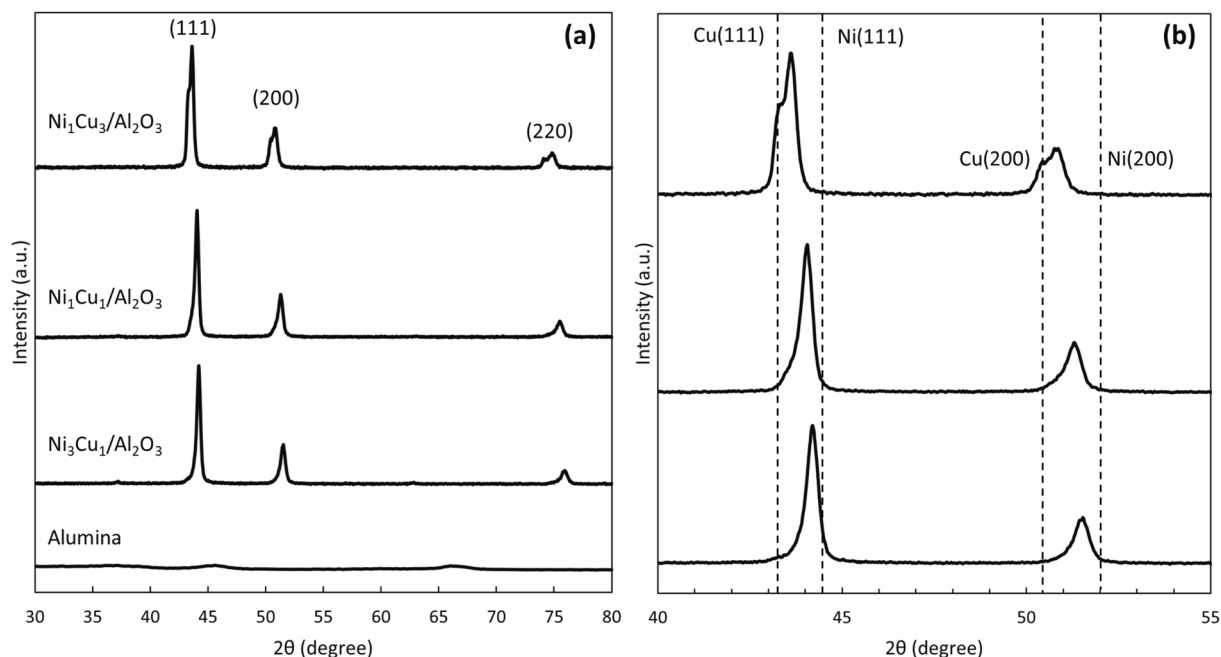


Fig. 5. XRD patterns of the alumina support and bimetallic Ni-Cu catalysts: (a) overall pattern, (b) zoomed in image of the 2θ range of $40^\circ - 55^\circ$.

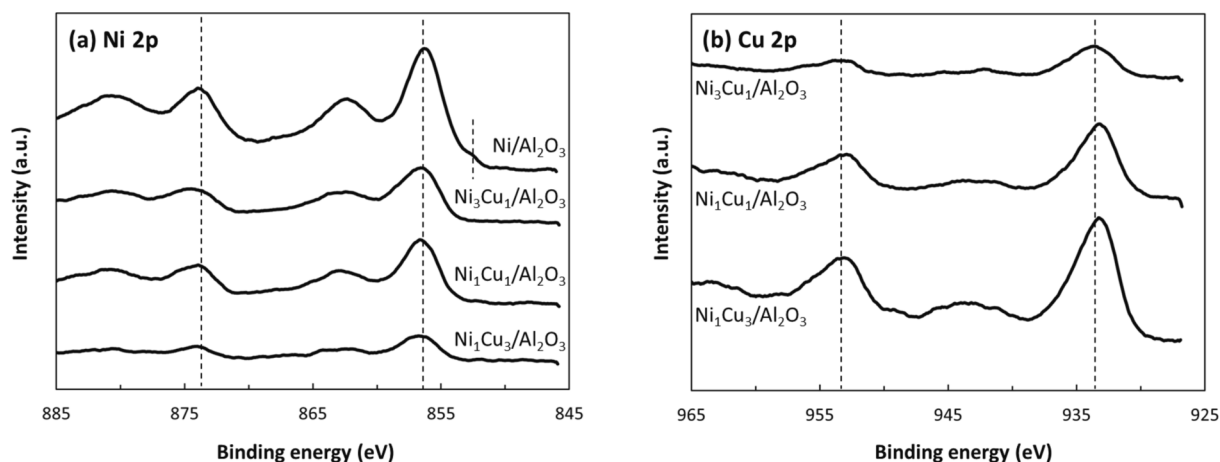


Fig. 6. XPS profiles of the monometallic $\text{Ni}/\text{Al}_2\text{O}_3$ and bimetallic Ni-Cu catalysts: (a) Ni 2p spectra, (b) Cu 2p spectra.

catalyst morphology.

3.3. Catalytic performance study for sorption-enhanced steam methane reforming

As discussed in section 3.2, both $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ and $\text{Ni}_1\text{Cu}_1/\text{Al}_2\text{O}_3$ 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 ($T = 600, 650$, and 700°C) and the corresponding CH_4 conversion (Equation (6)), H_2 yield (Equation (7)), H_2 purity (Equation (8)), and CO selectivity (Equation (9)) are presented in Fig. 8.

The influence of reaction temperature on the SESMR process is a combined effect of temperature on the SMR reaction (Equation (1)), the WGS reaction (Equation (2)), and the adsorption of CO_2 absorption by CaO (Equation (3)). As shown in Fig. 8 (a) and (b), both CH_4 conversion and H_2 yield increased with temperature, indicating that the effect of endothermic SMR offsets the negative impact of the exothermic

reactions in the temperature range of $600 - 700^\circ\text{C}$. Both $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{Cu}_1/\text{Al}_2\text{O}_3$ achieved very high CH_4 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 CO_2 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 CH_4 conversion and H_2 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 H_2 purity and CO selectivity (Fig. 7 (a) and (b)), both H_2 purity and CO selectivity slightly decreased as reaction temperature increased. This is due to the exothermic nature of the carbonation process – a CO_2 capture efficiency higher than 95 % can only be achieved at temperatures lower than 600°C [32].

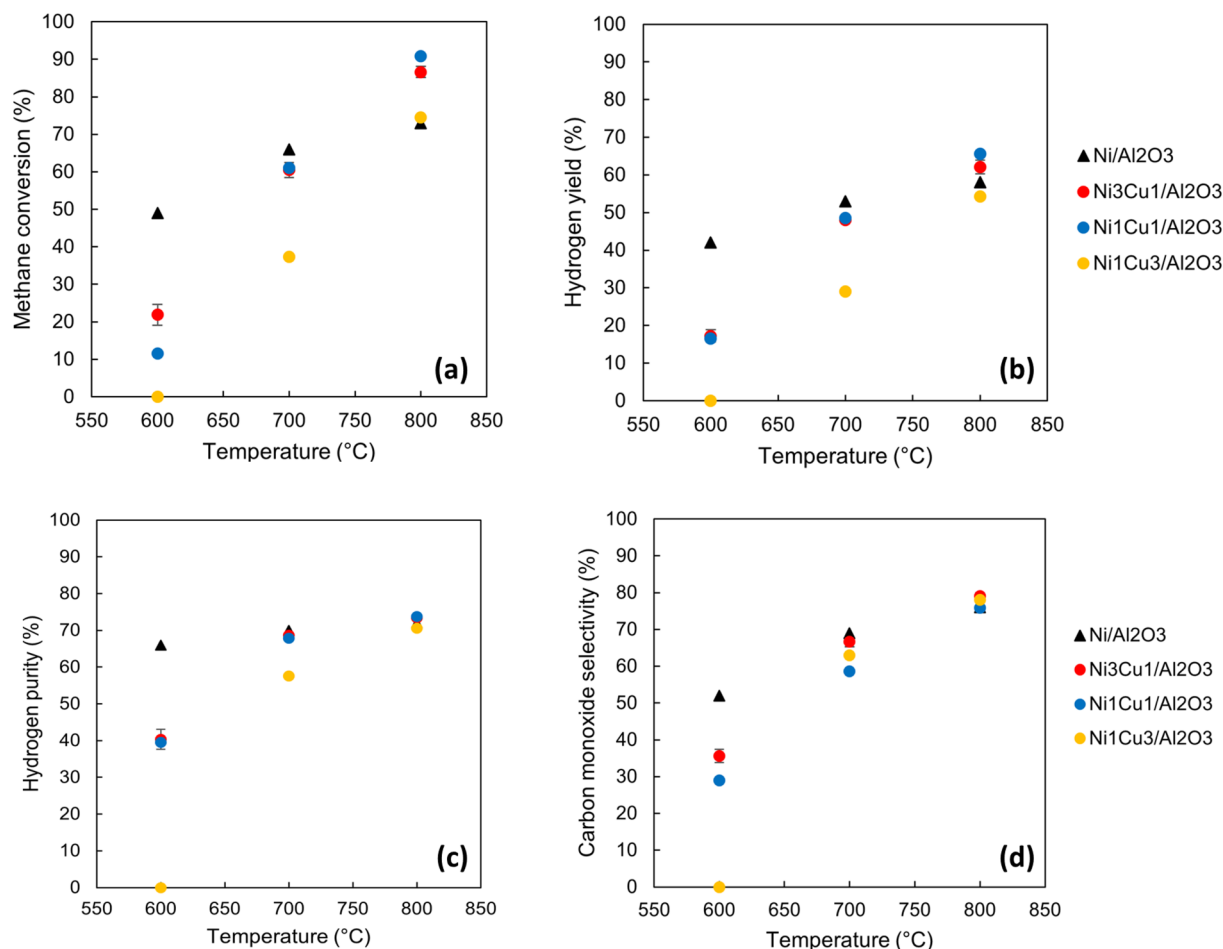


Fig. 7. (a) Methane conversion, (b) hydrogen yield, (c) hydrogen purity, and (d) CO selectivity of Ni/Al₂O₃ and the bimetallic Ni-Cu catalysts under SMR conditions.

Table 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)	Accumulative 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

Table 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

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 [33,34]. 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 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 5, the numbering system of the adsorption sites is detailed in Fig. 1. 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 [35,36]. 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 Ni₃Cu₁ and Ni₁Cu₁ are similar to pure Ni, whereas by increasing the concentration of Cu to 75 at.% (i.e. Ni₁Cu₃), the adsorption energies also increased. The same phenomenon was also reported by Alvarez-Garcia et al. [37], where the adsorption energies of CO₂ on Cu₃M₁, Cu₁M₁, and Cu₁M₃ (M = Ni, Pd, and Pt) were found to be

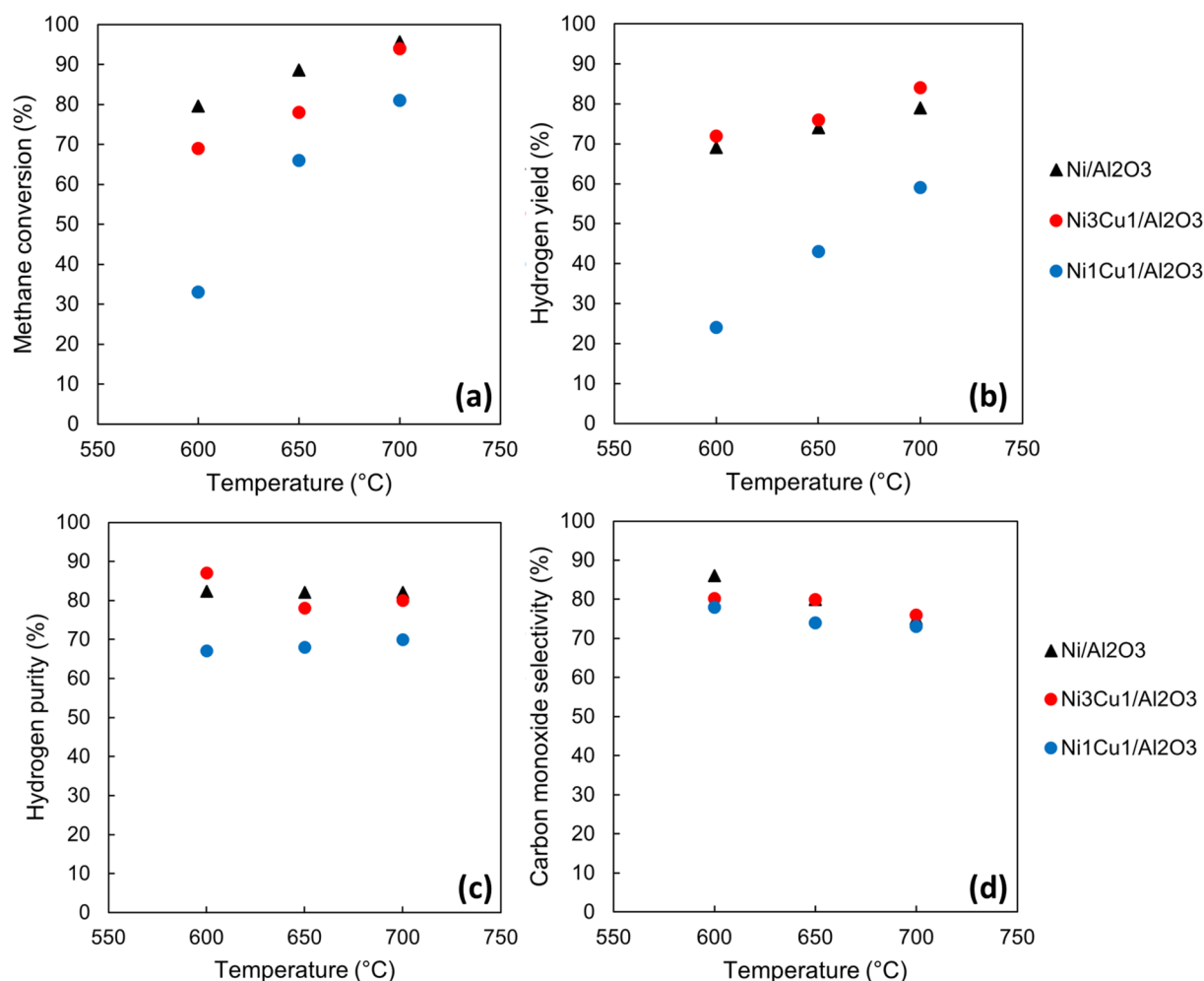


Fig. 8. (a) Methane conversion, (b) hydrogen yield, (c) hydrogen purity, and (d) CO selectivity of Ni/Al₂O₃ and the bimetallic Ni-Cu catalysts under SESMR conditions.

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.

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

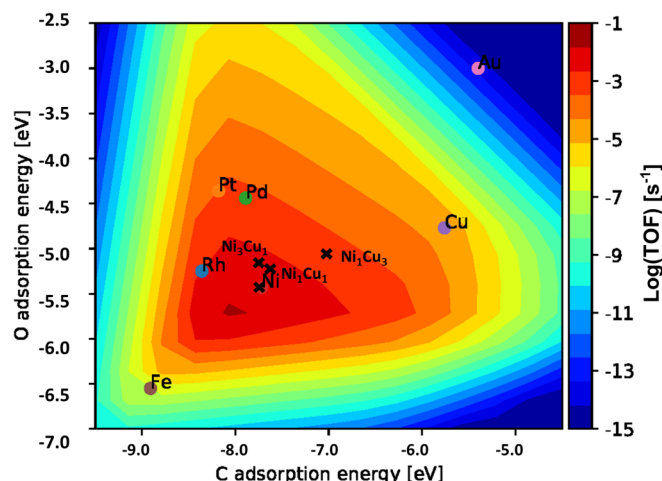


Fig. 9. TOF of H₂ production as a function of C and O adsorption energies.

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 (Fig. 9), 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 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 [38,39], the relatively low TOF of 10⁻³ s⁻¹ predicted for Ni₁Cu₃ is potentially due to its high C adsorption energy.

4. Conclusions

In this work, the performance of bimetallic Ni-Cu/Al₂O₃ catalysts

with different Cu loading levels (2.5, 5, and 7.5 wt%) was evaluated under both SMR and SESMR conditions, and compared with the conventional Ni/Al₂O₃ catalyst. Results from the SMR tests showed that all three bimetallic catalysts achieved higher methane conversion compared to Ni/Al₂O₃. The enhancement is most significant at 800 °C, with a methane conversion of approximately 90 % achieved by Ni₃Cu₁/Al₂O₃ and Ni₁Cu₁/Al₂O₃. The amount of coke formed on the used bimetallic catalysts was also found to decrease as Cu loading increases. 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 CO₂ 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 and cost-effective 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 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. It is also of interest to test the catalysts under multiple SESMR cycles with sorbent regeneration to evaluate the long-term activity and carbon resistance of the materials.

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Data Access Statement.

All data underlying the results are available as part of the article and in the [Supplementary Information](#) file.

CRediT authorship contribution statement

Siqi Wang: Writing – original draft, Investigation. **Ziqi Shen:** Writing – review & editing, Investigation. **Amin Osatiashtiani:** Resources. **Seyed Ali Nabavi:** Writing – review & editing. **Peter T. Clough:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/>.

Data availability

Data has been shared in the [Supplementary Information](#) file and in the main text

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Experimental and DFT study of (sorption-enhanced) steam methane reforming over bimetallic Ni-Cu catalysts

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