Cold plasma dielectric barrier discharge reactor for dry reforming of methane over Ni/γ-Al2O3-MgO nanocomposite

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ABSTRACT

Dry reforming of methane (DRM) to syngas in a dielectric barrier discharge (DBD) plasma reactor over Ni-loaded γ-Al2O3-MgO nanocomposite catalysts has been investigated. The catalysts are prepared by modified incipient wetness impregnation method, assisted by cold plasma treatment. The samples are characterized by XRD, N2 adsorption-desorption, H2-TPR, CO2-TPD, FESEM and EDX. The performance of the catalyst for DRM is evaluated at various specific input energy (SIE J ml\(^{-1}\)) and gas hourly space velocity (GHSV, h\(^{-1}\)). The maximum conversion achieved are 74.5% and 73% for CH\(_4\) and CO\(_2\) respectively, over 10% Ni/γ-Al2O3-MgO at specific input energy (SIE) = 300 J ml\(^{-1}\) and gas hourly space velocity (GHSV) = 364 h\(^{-1}\). The main reaction products are H\(_2\) (29.5%), CO (30.5%) with H\(_2\)/CO = 1 inferring RWGS reaction is suppressed for 12 h operation time. The enhanced conversion and yield are due to the strong metal-support interaction, high Lewis basicity and stable 10% Ni/γ-Al2O3-MgO catalyst as well as the plasma-catalyst interface. The energy efficiency (EE) of the plasma-catalytic DRM is higher (0.117 mmol kJ\(^{-1}\)) compared to plasma only (0.087 mmol kJ\(^{-1}\)) demonstrating the synergy between catalyst and plasma. The reaction mechanism is also proposed to postulate the steps involved in the DRM.

1. Introduction

The world is facing imminent energy crises due to urbanization and rapid increase in population. The energy supply is mainly based on fossil fuels (82%) while the rest 18% is produced from non-conventional energy resources [1]. It is essential to focus on renewable or non-conventional energy resources to reduce energy insecurity and endorse the concept of sustainable development. Utilization of fossil fuels caused emissions of greenhouse gases (GHGs), especially the major contributor, CO\(_2\) (76%) [1,2]. The second highest contributor is CH\(_4\) (16%), mainly emitted from agricultural activities, waste management, coal management and biomass burning or handling [3,4]. Utilization of CO\(_2\) and CH\(_4\) to produce syngas (CO, H\(_2\)) and other valuable chemicals in dry reforming of methane (DRM) (Eq. (1)) could improve the technology for increasing carbon efficiency. DRM produced syngas with the composition of H\(_2)/CO = 1\) which is the feedstock for Fischer-Tropsch (FT) synthesis to produced liquid fuels [5].

Several technologies in DRM such as photochemical, electrochemical and thermochemical pathways with or without catalyst, and all the possible combinations have been accomplished during the last two decades [5–7]. Recently, non-thermal plasma (NTP) for DRM has attracted many researchers. DRM is usually carried out using dielectric barrier discharge (DBD), but microwave plasma (MW) and gliding arc (GA) NTPs are uncommon in DRM [8,9]. However, MW and GA have higher energy efficiency (EE, mmol kJ\(^{-1}\)) as compared to DBD plasma in DRM as well as in CO\(_2\) splitting [2,10]. Nevertheless, the EE can be improved by using different potential heterogeneous catalysts for DBD plasma DRM, specifically called plasma-catalysis [11–13]. DBD plasma has some advantages for DRM since the energy input is low, with easy operation including catalyst loading and upscaling. DBD has a modest reactor design and also lower installation cost [10,14]. However, the major problems with DBD plasma DRM are lower energy efficiency and the deposition of surplus carbon due to the possible reactions such as methane cracking (Eq. (2)) and Boudouard reaction (Eq. (3)). The deposited carbon blocks the active site of catalyst, causing sintering of metal particles and deactivating the catalyst, as well as decreases the DRM process performance [15].

\[
\begin{align*}
    \text{CH}_4 + \text{CO}_2 & \leftrightarrow 2\text{CO} + 2\text{H}_2 & \Delta H^{298} &= 247 \text{ kJ mol}^{-1} \\
    \text{CH}_4 & \leftrightarrow \text{C} + 2\text{H}_2 & \Delta H^{298} &= 75 \text{ kJ mol}^{-1} \\
    2\text{CO} & \leftrightarrow \text{C} + \text{CO}_2 & \Delta H^{298} &= -172 \text{ kJ mol}^{-1}
\end{align*}
\]
Different types of catalysts have been synthesized for NTP DRM to enhance the plasma-catalytic performance and stability by inhibiting carbon deposition [16–18]. Noble metals and transition metals (Pt, La, Ce, Ru, Rh) catalysts have seemed preferable due to their better stability in DRM, but the high cost makes the noble metals unsuitable for commercial practice [19–21]. Ni-based catalyst is widely considered for plasma DRM due to availability and low cost. Regrettably, the Ni catalyst inevitably deactivated due to metal sintering and carbon deposition in NTP catalytic DRM [22,23]. The most common supports used in Ni-based catalysts are γ-Al2O3, MgO, ZnO, TiO2, ZrO2 and multi-elemental supports [24,25]. Ni supported Al2O3 has been extensively used and reported unstable in NTP catalytic DRM owing to the rapid coke formation and sintering of active phase [26]. The activity and stability of the Ni-based (Ni/Al2O3) catalyst can be improved with the addition of alkaline-earth metal oxides such as MgO and CaO [17]. Combination of Al-Mg based support has high potential to process feed gases in thermal DRM [26]. The addition of MgO to Ni/Al2O3 as a promoter assist to increase the basicity of the support as MgO is a strong basic oxide. MgO can also enhance the interaction of metal (Ni) and support (Al2O3) affects the reducibility and stability. With γ-Al2O3 having a high surface area and combined with MgO, a strong basic oxide, the composite catalyst can be suitable for NTP catalytic DRM [27]. DRM process is acidic in nature owing to the acidic properties of CO2; hence, the addition of MgO to γ-Al2O3 enhances the basicity and stability of the catalyst. It can further suppress the reverse water gas shift reaction (RWGS) (Eq. (4)) as well as the hydrogenation of CO2 (Sabatier reaction) towards methane and water formation (Eq. (5)). The strong basic sites allow adsorption and activation of high CO2 concentration on the support surface, thus increasing the CO2 conversion. Meanwhile, CH4 activation and dissociation are usually subject to plasma generated energetic species and active metal [28,29].

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298K} = +41.1 \text{ kJ mol}^{-1} \quad (4) \\
\text{CO}_2 + 4\text{H}_2 & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298K} = -164.9 \text{ kJ mol}^{-1} \quad (5)
\end{align*}
\]

Catalyst treatment and activation methods significantly affect the catalyst morphology and catalytic performance. Most recently, there is a certain focus on the synthesis of green catalyst by applying cold plasma for treatment to reduce metal ions into metal oxide and also to activate the catalyst other than by the conventional thermal calcination [30]. Liu et al. [30] studied the application of cold (DBD) plasma for catalyst treatment resulting in reduced particle size, improved metal dispersion and enhanced the metal-support interaction. DBD plasma treatment eliminated high energy consumption during high-temperature calcination and the reduction process [30]. In another development, Estifae et al. [31] studied the effect of plasma treatment (glow discharge) on catalyst morphology and DRM activity. It was reported that the plasma treated sample has 11% higher surface area, better activity and significant resistance to carbon deposition than a conventional calcined catalyst.

In light of the recent advancement in DBD plasma reactor for DRM, the synergy between catalyst and DBD reactor is still a major challenge. Zhang et al. [32] studied various material loading and the effect on catalytic activity, but the relation with discharge volume (V_D) and catalyst volume (V_cat) in a packed bed DBD system have not been considered. Recently, Tu et al. studied the promotional effect of Mg on Ni/Al2O3 in temperature controlled DBD reactor placed in a tube furnace, however, the insights of the reactor configuration based on V_cat and V_D was not elucidated as the discharge behaviour majorly based on catalyst loading and material behaviour. The DBD reactor configuration corresponding to a catalyst volume (V_cat) and discharge volume (V_D) is proportional to the feed flow rate of a packed-bed catalytic DBD plasma reactor. The relation between V_cat and V_D with corresponding to gas hourly space velocity (GHSV) in a packed-bed DBD reactor are useful in the selection of the appropriate catalyst loading, as it directly contributes to the energy efficiency (EE) of the catalytic DBD plasma DRM.

The aim of this work is to investigate the catalyst-plasma synergy in different DBD reactor configurations to enhance the energy efficiency. Ni/γ-Al2O3-MgO (Ni-AM) nanocomposites were synthesized by modifying incipient wetness impregnation method. The samples were then treated by DBD plasma to activate the catalyst for DBD plasma DRM. The catalysts were characterized by X-ray Diffraction (XRD), Brunauer–Emmett–Teller (BET), H2 temperature-programmed reduction (H2-TPR) and CO2 temperature-programmed desorption (CO2-TPD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX). The catalytic activity test was carried out in a packed-bed DBD plasma reactor. The effect of various Ni loadings, gas hourly space velocity (GHSV, h⁻¹) and specific input energy (SIE, ml kJ⁻¹) were further investigated for Ni-AM along with time on stream and carbon balance. The different reactor configurations based on V_cat and V_D corresponding to GHSV in a DBD plasma reactor has been critically analysed and reported. Furthermore, reaction mechanism has been proposed to rationalize the enhanced performance of Ni-AM.

2. Experimental

2.1. Catalyst preparation

Ni-based catalyst was prepared by modifying incipient wetness impregnation method followed by cold plasma treatment and activation.
as illustrated in Fig. 1(a–b). The γ-Al₂O₃ (99% Sigma Aldrich) and MgO (98% Sigma Aldrich) powder with a weight ratio of 2:1 were used as catalyst supports. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (99%, Sigma Aldrich) was dissolved in citric acid (99%) (Sigma Aldrich) solution and stirred for 10 min at 60 °C. γ-Al₂O₃ and MgO were added to a metal-citrate solution to enhance the metal dispersion over support surface and kept in vigorous stirring for 3 h at 110 °C [33]. Finally, the slurry was dried overnight in the oven at 110 °C.

The prepared samples were treated and calcined using cold DBD plasma (Fig. 1(b)). The prepared sample (2 g) was loaded in a quartz tube having 10 mm inner diameter wrapped with stainless steel mesh as a ground electrode. The stainless steel rod was inserted in the middle of quartz tube functioning as high voltage (HV) electrode. DBD plasma was supplied for 45 min, applying input power 100 W (SIE, 150 J ml⁻¹) with a frequency of 7.5 kHz for calcination and activation. The N₂ at a flow rate of 40 ml min⁻¹ was used for calcination and activation of the catalyst. The measured temperature was in the range of 280–300 °C at constant power. The temperature of the DBD plasma reactor was measured by using an infrared (IR) thermometer, Fluke 572-2 (Fluke Corporation USA). The catalysts turned blackish from bluish-white after measured by using an infrared (IR) thermometer, Fluke 572-2 (Fluke Corporation USA). The catalysts turned blackish from bluish-white after measuring the surface temperature with an infrared (IR) thermometer. Fluke 572-2. The catalysts turned blackish after activation. The 10 wt% Ni/Al₂O₃–MgO and 10 wt% Ni/γ-Al₂O₃–MgO were coded as Ni/A, Ni/M and Ni/AM respectively.

2.2. Material characterisation

The XRD patterns were obtained by the Rigaku Smart Lab, X-ray diffractometer (Rigaku Corporation, Japan) using Cu-ka radiation (40 keV, 40 mA) at a scanning rate of 1.2° min⁻¹ and scanning from 5°–90° of 2θ. The diffractometer was equipped with a Ni-filtered Cu-ka radiation source (I = 1.54056 Å), operated at 40 kV and 200 mA. The morphology of the prepared samples were examined before and after the DRM reaction by field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX). FE-SEM and EDX were conducted in Hitachi SU8020 (Hitachi High-Technologies Corporation, Japan) integrated with the beam of X-MaxN by Oxford Instrument optics and full control of the probe current from 1 pA to > 5 nA [34].

N₂ adsorption–desorption isotherms were recorded at 77 K on a Thermo Scientific Surfer Analyzer (Thermo Fisher Scientific, Italy). Prior to each analysis, the samples were degassed at 200 °C for 4 h to ensure complete removal of moisture. The Barrett–Joyner–Halenda (BJH) method was used to calculate the average pore diameter.

H₂–TPR was carried out to analyse the reduction profile of Ni in Micromeritic AutoChem II 2920 Chemisorption Analyzer (Micromeritics Instrument Corporation, USA). The catalyst (50 mg) was dried at 200 °C in the flow rate of 30 ml min⁻¹ helium gas (99.99%) in a quartz tube. The temperature was allowed to decrease to 50 °C and H₂/Ar (5%) gases flowed through the sample at a flow rate of 30 ml min⁻¹. Then, the catalyst was continuously heated at the rate of 10 °C min⁻¹ to 1000 °C. The signals for H₂ (m/e = 2) and H₂O (m/e = 18) were noted.

CO₂–TPD was conducted in a quartz tube on Al₂O₃ and Ni-AM fresh catalyst using Micromeritic AutoChem II 2920 Chemisorption Analyzer (Micromeritics Instrument Corporation, USA). 50 mg sample was pre-heated with He gas (30 ml min⁻¹) at 700 °C for 1 h and left to cool at room temperature. CO₂ was adsorbed at 50 °C for 1 h and weakly adsorbed CO₂ was removed by purging with H₂ at a flow rate of 30 ml min⁻¹. The sample was heated from 50 to 900 °C at the rate of 10 °C min⁻¹ in the flow of He gas and desorption of CO₂ was detected by TCD. CO₂ desorption amount was estimated by integrating TPD profile with distributing fitting software (BEL Japan).

2.3. DBD-plasma reactor setup

The schematic DBD plasma system is demonstrated in Fig. 2. The DBD system consists of four major parts: gas feeding system, alternating current (AC) power supply, plasma reactor and gas analysis system. The gas feeding system consisted of CH₄ and CO₂ gas cylinders, a gas mixer, and mass flow controllers (ALICAT Scientific 200 SCCM, USA) for both reactant gases. The AC power supply (CTP-2000K, China) was integrated with a voltage regulator (1–30 kV) to generate the plasma. The Tektronix TDS 102B two-channel digital oscilloscope with a high voltage probe (Tek P6015A) was used to assess the input voltage, frequency and total current. The alumina dielectric tube has a length of 35 cm with inner diameter 10 mm and outer diameter 12 mm. The catalyst was incorporated in the middle of the discharge zone packed with glass wool. A high voltage stainless steel electrode having a diameter of 4 mm and elongated ground electrode aluminium with length 20 cm was used to generate the plasma and DBD effect. The gas analysis system comprised of an online Gas Chromatograph (GC) (Agilent 6890N) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). A HP-PLOT capillary column (Agilent, 40 m × 0.53 mm ID, 40 μm) for detecting air and CO₂, one unit of Molsieve capillary column (Agilent, 30 m × 0.530 mm ID, 25 μm) for separating H₂, O₂, N₂, CH₄ and CO were connected to the TCD detector. In addition, one unit of HayeSep Q-Supelco, (6 ft × 1/8 in. ID × 2.1 mm OD, 80/100 mesh) for backflushing C₂ to C₆ was connected to the TCD. For separating C₁ to C₆ hydrocarbons, a unit of GS-GasPro (Agilent, 60 m × 0.32 mm ID) capillary column was connected to the FID detector.

CH₄ and CO₂ with purity of (99.9%) were used as feed gases with the feed ratio 1:1. Plasma power supply integrated with voltage regulator produced the plasma. Digital mass flow controllers measured the flow rates of the input gases. The reactor consisted of a high temperature and frequency resistant alumina tube, HV electrode inserted in the middle of an alumina tube and wrapped with the ground electrode. Two polytetrafluoroethylene (PTFE) end pieces were fitted at both ends of the reactor. Each end piece has a hole as gas inlet and outlet and one central hole for passing the high-voltage electrode. In the reactor configuration, two different approaches were made to study the relation between the length of the ground electrode, D₀, V₀ and Vcat. D₀ was varied (D₀ = 5–20 cm) to achieve different V₀ at the constant discharge gap (D₂gap) 3 mm. The effect of GHSV was studied in three different approaches. (i) Varying total flow rate at constant V₀ and Vcat (GHSV); (ii) V₀ was adjusted at constant Vcat and total flow rate (GHSV'); and (iii) catalyst bed volume (Vcat) varied at different catalyst loadings (0.5, 1, 2 g) at constant flow rate of reactant gases (GHSV'). The output flow rate was measured by a digital bubble flow meter and analysed by an online Gas Chromatograph (GC) equipped with TCD and FID.

2.4. Plasma-catalyst activity test

The plasma-catalytic activity tests were performed to analyse the performance of catalysts in DBD plasma DRM at atmospheric pressure and room temperature. The responses comprised of reactant conversion, selectivity, yield, carbon balance, and EE and were calculated according to Eqs. (6)–(16). The time on stream was tested to analyse the stability of the selected catalyst.

\[
\text{CH}_4\text{ conversion (X}_{\text{CH}_4}) \% = \left( \frac{(\text{nCH}_4)_{\text{in}} - (\text{nCH}_4)_{\text{out}}}{(\text{nCH}_4)_{\text{in}}} \times 100 \right) \tag{6}
\]

\[
\text{CO}_2\text{ conversion (X}_{\text{CO}_2}) \% = \left( \frac{(\text{nCO}_2)_{\text{in}} - (\text{nCO}_2)_{\text{out}}}{(\text{nCO}_2)_{\text{in}}} \times 100 \right) \tag{7}
\]

\[
\text{CO selectivity (S}_{\text{CO}} \% = \left( \frac{\text{nCO}_{\text{out}}}{(\text{nCH}_4)_{\text{in}} - (\text{nCH}_4)_{\text{out}} + (\text{nCO}_2)_{\text{in}} - (\text{nCO}_2)_{\text{out}}} \times 100 \right) \tag{8}
\]

\[
\text{H}_2\text{ selectivity (S}_{\text{H}_2} \% = \left( \frac{\text{nH}_2}_{\text{out}}{2 \times (\text{nCH}_4)_{\text{in}} - (\text{nCH}_4)_{\text{out}}} \times 100 \right) \tag{9}
\]
3. Results and discussion

3.1. Catalyst characterisation

XRD was carried out to identify crystallography of the prepared catalysts. Fig. 3 and Table 1 shows XRD patterns with detail crystallinity of Ni-A, Ni-M and Ni-AM after plasma treatment and activation of catalyst samples. The XRD patterns confirmed the formation of cubic crystalline phases of NiO, γ-Al₂O₃ and MgO. The γ-Al₂O₃ cubic phase (space group, Fd-3m (227)) is detected at 19.07°, 32.55°, 45.06° and 66.05° for faces (hkl) (100), (311), (400) and (440), respectively (JCPDS#50-0741). The NiO index peak appeared in 37.24°, 43.99° and 63.1° for face (hkl) (111), (200) and 220 respectively (JCPDS No. 44-1159) (space group, Fm-3m (225)) [37,38]. The crystallinity of MgO has been decreased with the addition of γ-Al₂O₃. MgO peaks, detected at 37.24°, 43.99°, 63.1° and 78.6°, correspond to hkl (200), (211) (222) and (311) (JCPDS No. 45-0946) (space group, Fm-3 m (225)) and are in good compromise with literature [12,27]. The weak peak concentration of Al₂O₃ in Ni-AM is perhaps due to cold plasma treatment (< 300 °C) [26]. The d-spacing and crystallite size are listed in Table 1 corresponding to the faces of Al₂O₃, NiO and MgO [39,40]. The average crystallite size is 12.3 nm, 13 nm and 15.5 nm for NiO, Al₂O₃ and MgO respectively.
isotherms, the higher N2 is adsorbed due to the capillary condensation. The pore size distribution of Ni-A, Ni-M and Ni-AM are categorized as mesoporous since the distribution of the pore size is mostly between 2 and 50 nm [43]. The surface area of Ni-A (119 m² g⁻¹) is higher than Ni-M (36 m² g⁻¹), whereas after combining in composite, the surface area of Ni-AM is 74 m² g⁻¹. The low surface area of Ni-AM as compared to Ni/A is ascribed to the Ni dispersion over support surface and it may block the pores, consequently, the MgO has also a lower surface area, which definitely reduced the surface area of composite Ni-AM. 

H₂-TPR was carried out to determine the interaction between Ni and support, as well as the reducibility of the active phase of the species and correlates to the DBD plasma treatment and activation. Fig. 6(a) shows TPR profile for the Ni-AM nanocomposite catalyst. The first two peaks at low temperature are attributed to the reduction of Ni²⁺ crystallites at 485 °C and 572 °C to NiO and interacting with support [12]. The low-temperature signals can also be attributed to the β-NiO interaction with Al₂O₃ and reduction of NiO-MgO. The second peak at high temperature is associated with γ-NiO at 904 °C to NiO and interprets the strong interaction with support [45,46]. The high-temperature peak is more resemblance to the γ-NiO having stronger interaction as compared to β-NiO [43]. The factors usually affect the nickel reduction are Ni loading, calcination temperature and interaction of NiO and support. In this case, samples are treated and activated using cold plasma rather than the conventional calcination and reduction methods to reduce the bulk nickel oxides. The reducibility of the Ni is improved by cold plasma decomposition and Ni atoms can diffuse into the support uniformly due to the cold plasma effect reported elsewhere [47]. The total H₂ uptake by Ni-AM at three different peaks are 40.19 μmol g⁻¹, 72.54 μmol g⁻¹ and 430.5 μmol g⁻¹ at 485.4 °C, 572 °C and 904.2 °C, respectively (Table 3).

The basicity of catalyst has significant influence in the catalytic activity in NTP DRM due to the acidic nature of CO₂ in the reaction. Strong basic sites can enhance the catalytic activity as CO₂ is acidic in nature and it increases the chemisorption and activation of reagent gas [29]. CO₂-TPD was carried out to analyse the basic sites of fresh Ni-AM and Al₂O₃ (control) catalyst as depicted in Fig. 6(b-c). A weak peak has been analysed at 50–200 °C against the TCD signal in column (I) for Al₂O₃ and Ni-AM. The lower temperature peaks indicate that the adsorbed CO₂ can be easily disabled from basic sites, inferring the Al₂O₃ has more weak basic sites than Ni-AM catalyst. The peak intensity of strong basic sites is much higher than lower temperature, weak basic sites in Ni-AM, as the CO₂ uptake by strong basic sites is much higher for Ni-AM as depicted in Table 3. The distribution of the basic sites, i.e. weak, intermediate, strong and very strong, on the catalyst corresponds to the peak within the temperature in the ranges of 20–150 °C, 150–300 °C, 300–450 °C and > 450 °C in CO₂-TPD profile [12,48]. The peaks show the strong basic sites in temperature ranges up to 200–500 °C in Ni-AM, while weak sites were analysed at 20–150 °C for Al₂O₃ indicating lower basicity. Furthermore, an elbow (peak) has been detected in both samples at 825 °C and 833.3 °C with CO₂ uptake was higher for Ni-AM than Al₂O₃ which has no significant CO₂ uptake. The

<table>
<thead>
<tr>
<th>2θ (degree)</th>
<th>hkl indices</th>
<th>d-spacing (nm)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>37.49</td>
<td>(111)</td>
<td>0.288</td>
</tr>
<tr>
<td>Ni-M</td>
<td>44.5</td>
<td>(200)</td>
<td>0.25</td>
</tr>
<tr>
<td>Ni-AM</td>
<td>63.99</td>
<td>(220)</td>
<td>0.176</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.07</td>
<td>(100)</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>32.55</td>
<td>(211)</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>45.06</td>
<td>(400)</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>66.05</td>
<td>(440)</td>
<td>0.14</td>
</tr>
<tr>
<td>Ni-AM</td>
<td>78.6</td>
<td>(311)</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 1

XRD analysis of the prepared fresh Ni-AM nanocomposite.

Fig. 4 demonstrates the FE-SEM micrographs of 10 wt% Ni-AM nanoparticles with different magnification to analyse the morphology and metal dispersion over catalyst support. Fig. 4(a) displays the nanoparticle uniform particle size in Ni-AM catalyst at 1.0 μm magnification. Ni-AM nanocatalyst demonstrates the homogeneous structure of the particles. Fig. 4(b) reveals uniform particle size and it assists in the metal dispersion to increase the active sites. The successful preparation of controlled morphology is due to the addition of citric acid as surfactant and cold plasma treatment [27,30,41].

Ni₂ adsorption-desorption isotherms of Ni-A, Ni-M and Ni-AM samples are demonstrated in Fig. 5(a). The samples of Ni-A and Ni-AM displays type IV isotherm with a hysteresis loop of H3 type, an indicative of mesoporous material [42]. However, Ni-M sample displays type II isotherm. The volume adsorbed at higher P/P⁰ caused by adsorption occurs by mesopores. The adsorption of N₂ is lower in low P/P⁰, which interprets the minimal formation of micropores in the samples. The Ni-AM samples depict the hysteresis (H3) loop. The hysteresis loop for Ni-AM is higher (non-identical) to that of Ni-A and Ni-M due to the distortion of Al and Mg crystal lattice. At higher P/P⁰ in type IV isotherms, the higher N₂ is adsorbed due to the capillary condensation below the expected condensation pressure of the N₂ [43]. According to the classification of IUPAC, the material shows H3 type hysteresis loop having mesoporous structure and the pores are interconnected to each other [44]. The pore size distribution of Ni-A, Ni-M and Ni-AM are presented in Fig. 5(b). The Ni-AM nanocomposite demonstrates the pore diameter of the sample is mostly between 5 and 30 nm with a high intensity of volume uptake, compared to Ni-A and Ni-M.

Table 2 describes the specific surface area, pore volume, pore diameter and average crystallite size of the prepared samples. The pore volume for Ni-A, Ni-M and Ni-AM samples were 0.242, 0.118 and 0.196 cm³ g⁻¹, respectively. Furthermore, the majority of the pore diameter culminates at 30 nm for all prepared samples. The pore diameter of Ni-M is higher as compared to Ni-A, while the nanocomposite Ni-AM displays a moderate BJH pore diameter. The reported samples are categorized as mesoporous since the distribution of the pore size is
strong Lewis basic sites have the capability of high CO₂ uptake and can inhibit carbon deposition in DRM.

3.2. Performance analysis of prepared catalysts

The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM. The performance of the Ni-A, Ni and Ni-AM catalysts were carried out in DRM.
out to analyse the DRM activity in the DBD plasma reactor and reported the results with 3% error margin. The conversion of CO₂ and CH₄ over different catalysts and product selectivity is depicted in Fig. 7(a). The CH₄ conversion of 74%, prevailed over 10 wt% Ni-AM nanocomposite compared to Ni/A, Ni/M and plasma only reaction. Ni-A and Ni-M conferred CH₄ conversion of 67.5% and 66%, respectively while for plasma only registers the lowest conversion (63%). Moreover, the CO₂ conversion was much higher in Ni-AM (73.5%) compared with Ni-A (64%) and Ni-M (65%), respectively. The CO₂ conversion in plasma only was recorded the lowest (59%). The higher conversions of CH₄ and CO₂ in Ni-AM nanocomposite as compared to Ni-A, Ni-M and plasma only DRM is attributed to the well-dispersed Ni on the catalyst surface and the basic nature of the composite catalyst due to the addition of MgO as a promoter [17]. As discussed in the CO₂-TPD analysis, strong basic sites exist in Ni-AM, that could enhance the chemisorption and activation of reactant gas resulting in high conversion. The presence of Ni in Ni/AM increased the active sites for the activation and dissociation of CH₄ in the plasma-catalyst DRM.

The H₂ selectivity is the highest over Ni/AM (46%) as compared to Ni/A (37%), Ni/M (37.5%) and plasma only (Fig. 7(a)). The CO selectivity is the following order: Ni/AM (47.5%) > Ni/A (43%) > Ni/M (40%) > plasma only (38%). Consequently, the ratio of H₂/CO was much lower than unity for Ni/A, Ni/M and plasma only. The H₂ and CO ratio obtained in Ni-AM was closed to unity (0.98) as shown in Fig. 7(b), suitable for FT synthesis for synthetic liquid fuels production [11,29,49]. Higher selectivity of CO in plasma only and Ni/A indicates the occurrence of RWGS (Eq. (4)) which utilizes H₂ and CO₂ to produce CO and H₂O [50]. The H₂/CO ratio in Ni-AM indicates RWGS is suppressed due to the highly basic nature of the catalyst. The formation of C₂ hydrocarbons (C₂H₆) is higher in plasma only and Ni-A which interprets the bulk formation and recombination of methyl radicals. However, Ni-AM enhances the H₂ production owing to the suppressed recombination of CH₃ and H species or possibly a further breakdown of C₂H₆ due to the electric field enhancement in the presence of a Ni/AM catalyst. The H₂ yield might be enhanced due to the chemical kinetic changes, as a consequence of significant heating of gas mixture in the
presence of a catalyst, since product distribution is highly dependent on gas temperature [51]. The EE is higher in Ni-AM (0.11 mmol kJ⁻¹) than Ni-A, Ni-M and plasma only DRM at the same experimental parameters. Thus, the Ni/AM catalyst is selected as the best catalyst for further parametric and reactor configuration study. Various Ni loadings (5, 10, 15 and 20 wt%) in AM catalyst support was tested to examine the effect of Ni content on the catalytic activity in DBD plasma for DRM as presented in Fig. 8. Increasing Ni loading, partly increases the conversions of CH₄ and CO₂ (Fig. 8(a)). The conversions of reactant gases in 5% Ni are lower than that of 10–20 wt% Ni loading. However, there is no significant improvement in the conversion of reactants in 15% Ni and 20% Ni as compared to 10% Ni loading. H₂ selectivity increases with Ni loading from 5 to 10 wt%, while marginally decreases over 15–20 wt% of Ni loading as shown in Fig. 8(b). More importantly, CO selectivity gradually increases probably due to oxidation of deposited carbon (Fig. 8(b)). The deposited carbon may be oxidized to CO by interacting with oxygen species that are generated from CO₂ and it is usually referred to as carbon gasification [52,53]. The conductive Ni active sites dispersed on the catalyst surface contributes to CH₄ dissociation to form a reactive carbon, which takes part in carbon gasification [28]. The selectivity of C₂H₄ is not significantly affected. The higher Ni content may lead to the formation of carbon since high Ni loading inhibits the dispersion of metal over support surface, and rate of monatomic carbon formation over gasification is expected to accumulate and promote filamentous carbon. Coke deposition is also dependent upon the different carbon formation routes and its oxidative removal [54,55]. Hence, the loading of active metal and its dispersion on support play a substantial role in the plasma-catalysis system.

3.3. Time on stream and carbon balance

The effect of the time on a stream of Ni-A, Ni-M and Ni-AM catalyst has been carried out for 12 h operation time at constant GHSV, feed ratio, V Ces and V D in DBD cold plasma reactor for DRM as shown in Fig. 9(a). After 12 h of operating time, the conversions of CH₄ and CO₂ decreased for Ni-A and Ni-M (Fig. 9(a)) due to coke formation through methane cracking and Boudouard reactions [31]. Ni-AM displays better stability compared to Ni/A and Ni/M in 12 h operation time. Fig. 9(b–c) indicated no severe reduction in selectivity and yield of CO and H₂ in Ni-AM. The high activity and stability of Ni-AM may be attributed to the high Lewis basicity as well as the high dispersion of active metal on γ-Al₂O₃–MgO due to the cold plasma treatment and activation [30]. The carbon balance (C₀) explains the carbon formation during the DRM process (Eq. (15)). Carbon deposition is lower (15%) for Ni/AM as compared to Ni/A and Ni/M during the operation time (12 h) for Ni-AM (Fig. 9(d)). Meanwhile, C₀ for Ni-A and Ni-M significantly dropped owing to the deposition of filamentous carbon [28]. The EE of the Ni-AM is higher than that of Ni-A and Ni-M, as depicted in Fig. 9(d), confers Ni-AM gave a better plasma-catalytic performance compared to Ni-A and Ni-M. Table 4 summarizes the comparison of the present study with previously reported literature for catalytic DBD reactor. The plasma-treated catalyst registers high conversion, selectivity and H₂: CO ratio close to unity – a requisite for subsequent syngas processing. The previous studies reported superior conversions and EE but the syngas composition (H₂: CO < 1) is less suitable for the gas to liquid technology (GTL) [18]. Furthermore, the different experimental conditions such as catalyst loading, reactor configuration (discharge volume, discharge gap, electrode morphology, etc.), and power input play a significant role in feed processing. The comparison in Table 4 presents the various experimental conditions affect the EE of DBD reactor.

The elemental distribution of spent alumina tube and catalyst (Ni-AM) are demonstrated using EDX. Fig. 10(a) exhibits carbon formation on the surface of the alumina reactor tube in plasma only DRM. The carbon formation in plasma only DRM was higher than coupling with nanocomposite Ni/AM depicted in elemental analysis. This interpretation is also supported by carbon balance (C₀). The carbon deposited on the catalyst is insignificant after the reaction (Fig. 10(b)). The sample comprised of O, Al and Mg with higher peak intensity in EDX analysis. While Ni and carbon showed lower intensity peaks in EDX chromatogram. MgO resisted carbon formation due to the strong basic nature, which promoted chemisorption and activation of CO₂ [56]. Active metal generated carbonaceous species, possibly via methane cracking, reacted with oxygen produced from CO₂ or CO and contributed to the low carbon formation.

3.4. Effect of specific input energy (SIE)

The effect of SIE was investigated for Ni-AM catalyst by varying the input power from 50 to 150 W adjusting the input voltage through a voltage regulator at constant applied frequency 7.5 kHz. The input power was adjusted by applying different applied voltages from 10 to 20 kV at constant GHSV, V Ces and V D. SIE is inversely proportional to EE. Fig. 11 depicts the effect of SIE (J ml⁻¹) on the catalytic activity of Ni-AM nanocomposite. The conversion of CH₄ and CO₂ increased while increasing the SIE by adjusting the input power at a constant feed flow rate. Increasing the input power could enhance electric field and electron density in discharge zone, hence endorsed the generation of active species, promote collision of active species with the reactant gases by altering the discharge behaviour and boost the dissociation process of CH₄ [28,57,58]. Furthermore, the conversion of CH₄ was partially higher than CO₂ due to the lower dissociation energy of CH₄ (4.5 eV) compared to CO₂ (5.5 eV) and higher threshold energy, 10 eV and 11.9 eV respectively [36]. The EE is decreasing while increasing the SIE in same experimental conditions. At SIE 150 J ml⁻¹ the EE is 0.128 mmol kJ⁻¹, while at 300 and 450 J ml⁻¹, the EE is recorded 0.117 mmol kJ⁻¹ and 0.105 mmol kJ⁻¹ respectively. The increment in the SIE also increases the conversion of reactant gases but the net effect on EE is not straightforward.

The selectivity of H₂ and CO increased with higher SIE; however, the C₂H₄ selectivity decreased. This suggests that the increase in SIE can change the reaction pathways and enhances the H₂ yield by suppressing the recombination CH₄ and H₂, or may assist the breakdown of methyl radicals [28]. The discharge behaviour and the conversion efficiency may also be changed due to the catalyst-plasma synergy. The synergistic effect can be easily achieved in plasma-catalysis as the plasma helps to intensify a surplus effect [59]. Plasma establishes a strong electric field and generates the reactive species, ions, electrons and photons to the surface and catalyst lowering the activation barrier for certain reactions [60]. The interaction between plasma-catalyst is interdependent, the effect of plasma changed the catalyst physio-chemical properties, while the catalyst modified the surface reactions by lowering the activation barrier and the discharge behaviour of plasma [59]. The plasma modifies catalyst properties such as dielectric constant, surface faceting and its morphology. Meanwhile, catalyst modifies the electric field generation, distribution and electron energy distribution, which consequently affects the generation of reactive species and promote the DRM activity [16]. Plasma-catalysis is a complex phenomenon to understand the effect of plasma and catalyst individually, but the synergistic effect is significant to distinguish the contribution of catalyst in DBD plasma catalysis [59].

3.5. Effect of GHSV

Feed flow rate is a significant operating process parameter for catalytic DBD plasma DRM, as it is directly related to the processing capacity of the DBD reactor and inversely related to the retention time of the reactants in the discharge zone [36]. The corresponding GHSV from feed flow rate can be calculated using Eq. (18). GHSV can be varied either by adjusting the total feed flow rate or reactor volume. However, in the plasma gas phase system, GHSV can also be calculated via two
approaches: based on reactor volume configuration; (i) discharge volume (VD) and (ii) catalyst bed volume (Vcat). Eq. (18) can be modified into (Eqs. (19)–(20)) for GHSV′ (h⁻¹) and GHSV″ (h⁻¹). The VD calculation for the DBD plasma reactor is reported in our previous work [36]. However, with the employment of catalyst, the VD will be changed and also affects the discharge behaviour of DBD plasma (Eq. (21)) [61]. The Vcat is calculated using Eq. (22). The bulk density (ρb) values are calculated by Eqs. (23) and (24).

\[
\text{GDHV (h⁻¹)} = \frac{\text{Total flow rate (cm}^3\text{ min}^{-1})}{\text{VD (cm}^3\text{)}} \times 60 \text{ min}^{-1} \times 1 \text{ h}
\]

\[
\text{GHSV′ (h⁻¹)} = \frac{\text{Total flow rate (cm}^3\text{ min}^{-1})}{\text{Vcat (cm}^3\text{)}} \times 60 \text{ min}^{-1} \times 1 \text{ h}
\]

\[
V_{\text{DF}} (\text{cm}^3) = (V_{\text{rate}} - V_{c} - V_{\text{cat}})
\]

\[
V_{\text{cat}} (\text{cm}^3) = \frac{\text{Mass of catalyst (g)}}{\text{Bulk density (g/cm}^3\text{)}} = \left(\frac{m_{\text{cat}}}{\rho_{\text{b}}}\right)
\]

\[
\rho_{\text{b}} (\text{g cm}^{-3}) = \rho_{\text{cat}} (1 - \varepsilon)
\]

### Table 4

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cat loading (g)</th>
<th>Flow rate (ml min⁻¹)</th>
<th>Power (W)</th>
<th>SIE (J ml⁻¹)</th>
<th>XCH₄ (%)</th>
<th>XCO₂ (%)</th>
<th>S_{H₂} (%)</th>
<th>S_{CO} (%)</th>
<th>H₂/CO</th>
<th>EE (mmol kJ⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%Ni/Al₂O₃-MgO</td>
<td>0.5</td>
<td>20</td>
<td>100</td>
<td>300</td>
<td>74.5</td>
<td>73</td>
<td>47</td>
<td>48</td>
<td>0.98</td>
<td>0.117</td>
<td>This studya</td>
</tr>
<tr>
<td>26%Ni/Al₂O₃</td>
<td>1.86</td>
<td>50.4</td>
<td>97</td>
<td>116</td>
<td>56.4</td>
<td>30.2</td>
<td>31</td>
<td>52.4</td>
<td>0.59</td>
<td>0.033</td>
<td>[28]</td>
</tr>
<tr>
<td>10%Ni/Al₂O₃</td>
<td>NA</td>
<td>50</td>
<td>50</td>
<td>60</td>
<td>38</td>
<td>21</td>
<td>27.6</td>
<td>45.3</td>
<td>0.61</td>
<td>0.72</td>
<td>[68]</td>
</tr>
<tr>
<td>10%Ni/Al₂O₃</td>
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<td>40</td>
<td>24</td>
<td>30</td>
<td>38</td>
<td>46</td>
<td>38</td>
<td>45</td>
<td>0.84</td>
<td>0.32</td>
<td>[69]</td>
</tr>
<tr>
<td>12%Co-Ni/Al₂O₃</td>
<td>0.1</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>56</td>
<td>30.2</td>
<td>31</td>
<td>52.4</td>
<td>0.60</td>
<td>NA</td>
<td>[70]</td>
</tr>
<tr>
<td>10%Ni/Al₂O₃</td>
<td>1.0</td>
<td>80</td>
<td>120</td>
<td>90</td>
<td>65</td>
<td>68</td>
<td>35</td>
<td>41</td>
<td>0.88</td>
<td>NA</td>
<td>[71]</td>
</tr>
</tbody>
</table>

*a* Experimental conditions: CO₂/CH₄ = 1, GHSV 364 h⁻¹, SIE = 300 J ml⁻¹, catalyst loading = 0.5 g, Vcat = 2.75 cm³, Dgap = 3 mm, Dc = 20 cm.
where \( V_\text{total} \) is total makeup volume and \( V_\text{cat} \) is the volume of catalyst.

In the first case, the effect of total feed flow rate (10–50 ml min\(^{-1}\)) corresponding to GHSV (h\(^{-1}\)) was investigated for Ni-AM in DBD plasma reactor at constant SIE, \( V_\text{cat} \), \( V_D \) and feed ratio 1:1 and the results are presented in Fig. 12. Increasing GHSV at constant \( V_\text{cat} \) and \( V_D \) decreased the conversion of CH\(_4\) and CO\(_2\) abruptly. The maximum conversion was achieved at the lowest GHSV. Increasing the GHSV at constant \( V_\text{cat} \) and \( V_D \) led to less interaction between reactants and reactive species due to shorter retention time. Evidently, the conversion of CO\(_2\) and CH\(_4\) declined from 75% to below than 50%, when increasing the feed flow rate from 10 to 50 (ml min\(^{-1}\)) for both reactant gases. The retention time is calculated by dividing the reactor volume over total flow rate [36].

Mass transfer limitations in gas phase catalytic reactions could be overcome using higher feed flow rates corresponding to GHSV at constant \( V_\text{cat} \) and \( V_D \). The effect of higher feed flow rate is more significant in the catalytic activity than that of mass transfer limitations due to shorter residence time [62]. The mass transfer limitation may also be reduced by surface modification of catalyst due to reactive species generated by plasma. The adsorbed reactive species of C and methyl radicals can be further oxidized by oxygen species to form CO and H\(_2\) [32]. The specific energy density decreased with increasing feed flow rate at constant input power. Hence, the conversion was heavily affected by the lower electron density and retention time. The influence of feed flow rate on the selectivity of H\(_2\) and CO was insignificant. At higher GHSV, the dissociation probability of reactants and energetic species may reduce and drops the conversions of reactant gases. However, CO and H\(_2\) are mainly produced from CO\(_2\) dissociation and H atom recombination [63]. The formation of methyl radicals increased at a shorter residence time, consequently increased the C\(_2\)H\(_6\) selectivity.

In the second case, GHSV is calculated based on \( V_\text{cat} \) and \( V_D \) expressed in Eqs. (19)–(20). Two different reactor configurations have been made in this study to investigate the effect of GHSV corresponding to \( V_0 \) (GHSV\(^v\)) and \( V_\text{cat} \) (GHSV\(^c\)) as illustrated in Figs. 13–14 and summarized in Table 5. Meanwhile, variation in GHSV corresponding to \( V_0 \) marked lower conversions and selectivity (Fig. 13(a)) due to shorter residence time and limited surface reaction, since \( V_\text{cat} \) (catalyst
loading) is constant. The electric field generated at constant \( V_{\text{cat}} \) is also not uniform. Furthermore, the effect of \( V_{\text{cat}} \) and \( V_D \) variation on the conversion of reactants was studied simultaneously. The conversion decreased while increasing GHSV for both cases (Fig. 14). However, high \( V_{\text{cat}} \) increases the conversion more than \( V_D \) due to more active sites, longer residence time and effective surface reactions. Higher \( V_{\text{cat}} \) led to the formation of strong electric field and electron density that exhibits different discharge behaviour [32]. Conversions of reactant gases at various GHSV were monitored for both reactor configurations based on \( V_{\text{cat}} \) and \( V_D \) respectively. Thus, it is imperative to understand the contribution of catalyst and plasma in a DBD reactor to get the synergistic effect. The EE in the reactor configuration based on \( V_{\text{cat}} \) is higher than those values in Table 5. There is a remarkable influence of catalyst loading on EE as the plasma discharge behaviour, electron density and electric field varied with different reactor configuration. The synergistic effect between plasma-catalyst gives additional effect and has been validated by EE in DBD reactor.

### 3.6. Reaction mechanism

Dry reforming of methane (DRM) at NTP is highly endothermic reaction requiring high energy input to activate, ionize and dissociate stable GHGs i.e. CO2 and CH4. DRM process can be further elaborated to understand the reaction mechanism during the application of cold plasma. The electron impact reactions such as electron impact excitation, ionization and dissociation are responsible for the gas breakdown in DBD plasma. In DBD plasma, threshold energy for electron impact ionization is too high to generate secondary electron, hence the electron impact excitation and dissociation play key role in DRM [30]. The threshold energy for direct dissociation of CH4 (10 eV) and CO2 (11.9 eV), certainly enough for vibrational excitation and dissociation of CH4 and CO2 to radicals because the average electron energy of DBD is lower. The electron dissociation energy of C-H (4.5 eV) and C-O (5.5 eV) are lower than the energetic electron energy (> 10 eV), which proposes the temperature of the electron (\( T_e \)) is much higher than gas temperature (\( T_g \)) (\( T_e > T_g \) [64]). The energetic electron collision is a
key factor to initiates the vibrational excitation and direct dissociation process of gas molecules and the formation of radicals CH_x*, CH_y*, CH_z*, H* and C species in the presence of a catalyst. The CO_2 dissociates mostly into CO*, CO and O* species [51,65]. The possible reactions according to product distribution are stated in Eqs.(25) and H. CH_x further dissociates into H and reactive carbon, which can be surface) on basic catalyst support can be attributed to high CO2 adsorption. Consequently, the adsorbed CO2 on the surface can react with the formation of H and reactive carbon. Moreover, carbon deposition reduced due to the oxidation of highly reactive oxygen species with adsorbed reactive carbon. The oxidative capability of basic supports is better than acidic and inert supports in NTP based DRM process. The higher Lewis basicity of the surface may lead to the absorption of CO2 and higher oxidation ability to reduce carbon deposition.

\[
\text{Methane dissociation}
\]

\[
e^- + CH_4 \rightarrow CH_3^* + H^+ + e^-
\]  \( \text{(25)} \)

\[
e^- + CH_4 \rightarrow C + 2H_2 + e^-
\]  \( \text{(26)} \)

\[
e^- + CH_4 \rightarrow CH_3^* + H_2 + e^-
\]  \( \text{(27)} \)

\[
e^- + CH_4 \rightarrow CH^* + H_2 + H^+ + e^-
\]  \( \text{(28)} \)

\[
e^- + CH \rightarrow C + H^* + e^-
\]  \( \text{(29)} \)

\[
CH^* + CH_4 \rightarrow C_2H_4 + H^*
\]  \( \text{(30)} \)

\[
H^* + H^* \rightarrow H_2
\]  \( \text{(31)} \)

\[
CH_3^* + CH_3^* \rightarrow C_2H_6
\]  \( \text{(32)} \)

\[
H^* + C_2H_6 \rightarrow C_2H_5^* + H_2
\]  \( \text{(33)} \)

The formation reactions can occur and formed higher hydrocarbons like C2-C4 during this process [58]. The recombination of H* species generates H_2 (Eq. (31)).

\[
\text{Carbon dioxide dissociation}
\]

\[
e^- + CO_2 \rightarrow CO^* + O^-
\]  \( \text{(34)} \)

\[
e^- + CO_2 \rightarrow CO + O + e^-
\]  \( \text{(35)} \)

\[
e^- + CO_2 \rightarrow CO_2^* + e^-
\]  \( \text{(36)} \)

The incorporation of catalyst in the discharge gas alters the discharge behaviour of the plasma by enhancing the electric field and promoting the reactive species generation. The plasma generated reactive species can also modify the catalyst surface. The excited species of reactant gases are randomly adsorbed on the catalyst surface and easily recombinated to further generate H_2 and CO. The surface chemistry in plasma-catalysis (Eqs.(37)-(42)) (M = active metal and S = support surface) on basic catalyst support can be attributed to high CO2 adsorption. Consequently, the adsorbed CO2 on the surface can react with O^-2 forms CO_3^2- that is highly reactive species. CO_3^2- can react with H atoms dissociated from CH_4 [66]. The CH_4 adsorption and dissociation take place on the surface of active metal as the excited species increases the vibrational temperature of CH_4 (Eq. (33)). It enhances the dissociative chemisorption of CH_4 on metal (Ni) surface to CH_3 (x = 1–3) and H. CH_4 further dissociates into H and reactive carbon, which can be oxidized by oxygen atoms. The complete reaction mechanism scheme of plasma-catalysis is shown in Fig. 15 for Ni-AM catalyst and Eqs. (38)-(42). The proposed reaction paths follow the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism whereby the CH_4 activation is on Ni and deposited C may gasify on MgO [48,67]. According to the proposed mechanism, the dissociation, or activation of CH_4 and CO_2 initiated by plasma, followed by the adsorption of elemental and intermedinates containing C, H, O and oxy-carbonates on the active sites and surface of the support. The surface reactions formed the desired products in the plasma-catalytic DRM.

\[
CH_4 + Ni + S \rightarrow NiCH_3 + Ni - H
\]  \( \text{(37)} \)

\[
2H - Ni \rightarrow H_2 + Ni
\]  \( \text{(38)} \)

\[
CO_2 + S \rightarrow CO_2 - S
\]  \( \text{(39)} \)

\[
CO_2 - S + O^-2 \rightarrow CO_2^* - S
\]  \( \text{(40)} \)

\[
CO_2^* - S + 2H_2 \rightarrow HCO_2^- - S + OH^- - S
\]  \( \text{(41)} \)

\[
CO - S \rightarrow CO + S
\]  \( \text{(42)} \)

The application of high Lewis basic support enhanced the CO2 chemisorption capacity and potentially higher CO2 conversion was observed [19,50]. It also adsorbs the excited methyl radicals, which may later lead to the formation of H and reactive carbon. Moreover, carbon deposition reduced due to the oxidation of highly reactive oxygen species with adsorbed reactive carbon. The oxidative capability of basic supports is better than acidic and inert supports in NTP based DRM process. The higher Lewis basicity of the surface may lead to the absorption of CO2 and higher oxidation ability to reduce carbon deposition.

4. Conclusion

The cold plasma treated Ni-AM catalyst is highly resistant to coke formation and prevailed high performance in a packed-bed DBD plasma DRM as compared to plasma only DRM. The low carbon deposition in Ni/AM as compared to Ni/A and Ni/M is attributed to high Lewis basicity, surface faceting and high dispersion of active metal. The H_2/CO ratio is about unity for Ni-AM catalyst indicated the lower formation of carbon by suppressing RWGS and carbon gasification. The enhanced H_2 is attributed to the suppression of recombination of CH_4 and H to form CH_4. Furthermore, Ni loading, SIE and GHSV (w.r.t reactor volume) are investigated as process parameters. The GHSV is exclusively studied in two different reactor configurations based on Vcat and V_D at a constant flow rate and its effect on the DRM activity is critically reported. The different conversion behaviour has been observed in both reactor configurations due to different discharge behaviour; selectivity was significantly affected while changing the GHSV in both approaches. The incorporation of catalyst in a packed bed plasma reactor caused synergetic effect as evident in the study of GHSV corresponding to Vcat and V_D. EE achieved for Ni-AM is 0.117 mmol kJ^-1 as compared to non-catalytic DBD DRM attested the synergy between plasma and catalyst. The outcome of this study is useful for evaluating and determining the contribution of GHSV in enhancing the EE of the catalytic DBD plasma reactor.
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