

# Thermal dry reforming of methane over La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst for hydrogen-rich syngas **production**

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# **Abstract**

The excess emission of greenhouse gases (GHGs) such as  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$  is posing an acute threat to the environment, and efficient ways are being sought to utilize GHGs to produce syngas  $(H_2, CO)$  and lighter hydrocarbons (HCs). In this study, the dry reforming of methane (DRM) has been carried out at 700 °C using  $La<sub>2</sub>O<sub>3</sub>$ co-supported  $Ni/MgAl<sub>2</sub>O<sub>4</sub>$  nano-catalyst in a fixed bed thermal reactor. The catalyst is characterized using various techniques such as XRD, FESEM, EDX-mapping,  $CO_2$ -TPD, H<sub>2</sub>-TPR and TGA. The modified MgAl<sub>2</sub>O<sub>4</sub> shows the flake type structure after the addition of  $La<sub>2</sub>O<sub>3</sub>$ . The TPR and TPD analysis shows the highly dispersed metal and strong basic nature of the catalyst consequently enhances the conversion of  $CO_2$  and CH<sub>4</sub>. The highest conversion for CH<sub>4</sub> is 87.3% while  $CO_2$  conversion is nearly 89.5% in 20 h of operation time. The selectivity of  $H_2$  and CO approached  $50\%$  making the H<sub>2</sub>/CO ratio above unity. In the longer time-on-stream (TOS) test, the catalyst shows elevated potential for longer runs showcasing better catalytic activity. The stability of the catalyst is indicated via a proposed reaction mechanism for DRM in operating conditions. Moreover, TGA indicates the lower weight loss of spent catalyst which ascribed the lower formation of carbon during TOS 20 h.

**Keywords** Dry reforming of methane  $\cdot$  thermal reactor  $\cdot$  MgAl<sub>2</sub>O<sub>4</sub>  $\cdot$  H<sub>2</sub> production  $\cdot$ syngas

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### **Introduction**

Dry reforming of methane (DRM) (Eq. [1](#page-1-0)) is an important technique which has been used to convert the greenhouse gases such as  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$  to syngas (H<sub>2</sub>, CO) and lighter hydrocarbons  $(C_2-C_3)$  [[1\]](#page-14-0). The syngas can be used as feedstock for the wellknown Fischer–Tropsch (FT) synthesis process in gas-to-liquid fuel technology [[2\]](#page-14-1). The CH<sub>4</sub> and CO<sub>2</sub> have been successfully converted into fuels via DRM [\[3](#page-14-2)], however, the carbon deposition is a major concern identifed in the recent studies [\[4](#page-14-3), [5\]](#page-14-4). Mainly, the carbon is formed via two famous reactions which are methane cracking (Eq. [2\)](#page-1-1) and Boudouard reaction (Eq. [3](#page-1-2)) [[6\]](#page-14-5). Another issue is the  $H<sub>2</sub>/CO$  ratio, which is usually less than unity due to the reverse water gas shift reaction (RWGS) (Eq. [4](#page-1-3)) [\[7](#page-14-6), [8](#page-14-7)].

$$
CH_4 + CO_2 \rightarrow 2 CO + 2 H_2 \Delta H^{\circ} = 247 \text{kJ mol}^{-1} \text{ (DRM)}
$$
 (1)

<span id="page-1-2"></span><span id="page-1-1"></span><span id="page-1-0"></span>
$$
CH_4 \to C + H_2 \Delta H^{\circ} = 75 \text{kJ mol}^{-1} \text{ (Methane cracking)} \tag{2}
$$

$$
2\text{CO} \rightarrow \text{C} + \text{CO}_2 \,\Delta H^\circ = -172 \,\text{kJ} \,\text{mol}^{-1} \,\text{(Boudouard reaction)}\tag{3}
$$

<span id="page-1-3"></span>
$$
CO_2 + H_2 \rightarrow CO + H_2O \Delta H^{\circ} = 41.27 \text{ kJ mol}^{-1} \text{ (RWGS)}
$$
 (4)

The aim of developing an efficient and stable catalyst is to improve the conversion efficiency, stability and  $H<sub>2</sub>/CO$  ratio with lower carbon formation [[9\]](#page-14-8). Various catalyst systems were employed to improve the conversion efficiency. The Nibased catalyst with various supports such as  $Al_2O_3$  [[10\]](#page-14-9), MgAl<sub>2</sub>O<sub>4</sub> [\[11](#page-14-10)], SiO<sub>2</sub> [[12\]](#page-14-11), Mesoporous silica molecular sieves (MCM) [[13\]](#page-14-12), MgO [[14\]](#page-14-13), zeolites [[15\]](#page-14-14) and  $ZrO<sub>2</sub>$ [\[16](#page-14-15)] were reported for DRM [[17\]](#page-14-16). Furthermore, co-supported catalysts were also extensively studied with multiple objectives such as  $CO<sub>2</sub>$  adsorption and metal dispersion [[14,](#page-14-13) [18](#page-15-0)]. The noble metals demonstrate high catalytic activity as well as inhibit the coke formation reported in the literature. However, the high cost makes them less suitable for the commercialization of the DRM process, extensively compiled by Pakhare & Spivey [[19\]](#page-15-1).

The Ni-based catalysts need further improvements to make them more viable for the DRM as the carbon growth on Ni sites is the most common issue with the singlesupported catalyst. Recently, the co-support system with Ni as active metal is seeking remarkable attention such as  $\text{Al}_2\text{O}_3$ -MgO [\[20](#page-15-2)]. To achieve the communal effect of both Al and Mg, the Ni/MgAl<sub>2</sub>O<sub>4</sub> spinel has been synthesized for DRM, and it resulted in a stable and enhanced performance than  $Ni/Al<sub>2</sub>O<sub>3</sub>$ . However, issues such as carbon formation and  $H<sub>2</sub>/CO$  ratio were not resolved [[21,](#page-15-3) [22\]](#page-15-4). The catalyst performance in the DRM also depends on the physicochemical properties of the material. The physicochemical properties of catalyst can be modifed by the preparation techniques and by introducing a co-support which will improve the basicity and metal dispersion on the catalyst support [\[23](#page-15-5)[–25](#page-15-6)]. The basic nature of the catalyst is also important for carbon deposition and deactivation of the catalytic performance [[26,](#page-15-7) [27](#page-15-8)]. Ni interface with MgAl<sub>2</sub>O<sub>4</sub> is improved by the communal effect of MgAl<sub>2</sub>O<sub>4</sub> and  $La_2O_3$  as mixed matrix support [\[28](#page-15-9)]. In thermo-catalytic DRM, the combined effect of  $La_2O_3$  and MgAl<sub>2</sub>O<sub>4</sub> catalyst is barely reported [[29\]](#page-15-10).

Herein, we investigate the Ni/La-Mg catalyst for high-temperature DRM to analyse the catalytic activity, products distribution and stability during the long-term continuous operation. We prepared the mixed-matrix support nano-catalyst of 10 wt.%  $Ni/La_2O_3-MgAl_2O_4$  and tested for DRM in a fixed bed thermal reactor. The catalyst material was characterized by X-ray difraction (XRD), feld emission electron microscopy (FESEM),  $H_2$  temperature-programmed reduction ( $H_2$ -TPR),  $CO_2$ temperature-programmed desorption ( $CO_2$ -TPD), N<sub>2</sub> adsorption–desorption (BET) EDX-mapping and TGA. Finally, a probable reaction mechanism was proposed based on product distribution.

### **Materials and methods**

#### **Material synthesis and characterization**

 $MgAl<sub>2</sub>O<sub>4</sub>$  and  $La<sub>2</sub>O<sub>3</sub>$  spinal was prepared by modifying the co-precipitation method followed by hydrothermal process reported elsewhere [[30\]](#page-15-11). For  $MgAl_2O<sub>4</sub>$  the respective nitrate salts were added to ammonia solution with a ratio of 2:1 (Al: Mg). The required quantities of citric acid and dimethylformamide (DMF) were added to improve the metal dispersion and better crystal growth. The solution was kept at 160 °C for 24 h in an autoclave for the hydrothermal process. The slurry was then washed several times using ethanol and DI water, and the samples were dried in an oven. The same method is repeated for the synthesis of  $La<sub>2</sub>O<sub>3</sub>$ . For co-support,  $MgAl<sub>2</sub>O<sub>4</sub>$  and  $La<sub>2</sub>O<sub>3</sub>$  were taken as 4:1 (wt. ratio) as co-support and prepared by microemulsion technique [\[31](#page-15-12)]. The  $10\%$  wt. Ni as the active metal was impregnated by the modifed incipient wetness impregnation method [\[32](#page-15-13)]. The catalyst was then calcined at 700  $\degree$ C for 3 h in a muffle furnace. The material was characterized by  $XRD$ , FESEM, H<sub>2</sub>-TPR, CO<sub>2</sub>-TPD, EDX-mapping, BET and TGA. The characterization methods and equipment details were reported elsewhere [\[32](#page-15-13)]. The crystallography and morphology of the catalyst were analysed by XRD, FESEM and BET. The crystallite size was calculated using the Scherrer equation [[32,](#page-15-13) [33](#page-15-14)]. The metalsupport interaction and basicity of the materials were analysed by TPR and TPD, and TGA was used to explain the thermal stability of the synthesized material.

#### **Experimental setup and calculations**

The experimental setup for the fxed-bed thermal reactor is presented in Fig. [1](#page-3-0). Briefy, the feed gases CH<sub>4</sub> (99.99%) and CO<sub>2</sub> (99.99%) controlled by a mass flow controller (ALICAT) were provided to the fxed bed reactor. The fxed-bed reactor consists of a vertical furnace (Carbolite UK) integrated with a thermocouple. The catalyst is loaded in alumina tube (10 mm inner diameter) with the help of quartz wool. A condenser and silica-bed are used to separate the liquid and gaseous products, respectively, before sending the syngas to the gas analysis systems. The products gases were analysed using



<span id="page-3-0"></span>**Fig. 1** Experimental setup for thermal catalytic dry reforming of methane

an online gas chromatograph (GC) (Agilent 6890 N) equipped with a thermal conductivity detector (TCD) and fame ionization detector (FID) [[29](#page-15-10)].

The catalytic activity tests were conducted to analyse the performance of the DRM catalyst in a fixed-bed thermal reactor. The reactant conversion  $(X)$  and selectivity  $(S)$ were calculated according to Eqs. ([5](#page-3-1)[–9](#page-3-2)). When *n* represents the number of moles of the individual species. The experiments were repeated twice to determine the relative error.

<span id="page-3-1"></span>
$$
CH_4 \text{ conversion } (X_{CH_4})\% = \left[ \frac{(nCH_4)_{\text{converted}}}{(nCH_4)_{\text{feed}}} \times 100 \right]
$$
 (5)

$$
CO_2 \text{ conversion } (X_{CO_2})\% = \left[ \frac{(\text{n CO}_2)_{\text{converted}}}{(\text{n CO}_2)_{\text{feed}}} \times 100 \right] \tag{6}
$$

$$
CO \text{ selectivity } (S_{CO})\% = \left[ \frac{(nCO) \text{ produced}}{(nCH_4 + nCO_2)_{\text{converted}}} \times 100 \right] \tag{7}
$$

<span id="page-3-2"></span>
$$
H_2 \text{ selectivity } (S_{H_2})\% = \left[ \frac{(nH_2)_{\text{produced}}}{(2 \times nCH_4)_{\text{converted}}} \times 100 \right]
$$
 (8)

$$
C_2H_6 \text{ selectivity } (S_{C_2H_6})\% = \left[\frac{(2 \times nC_2H_6)_{\text{produced}}}{(nCH_4 + nCO_2)_{\text{converted}}} \times 100\right]
$$
(9)

## **Results and discussion**

### **Physicochemical properties of the material**

The crystallographic structure of the prepared catalysts was analysed by X-ray diffraction (XRD) as shown in Fig. [2](#page-4-0)a. The X-ray diffraction peaks for  $MgAl_2O<sub>4</sub>$ 



<span id="page-4-0"></span>**Fig. 2 a** XRD of the prepared samples **b**  $H_2$ -TPR with inset  $H_2$  uptake profile and

(PDF#72–6947) were analysed, and the cubical phase (hkl; 311) was confrmed at 38.5° with a space group of 227: Fd3m [\[24](#page-15-15), [34\]](#page-15-16). The average crystallite size for  $MgAl<sub>2</sub>O<sub>4</sub>$  was 10.5 nm. Similarly,  $La<sub>2</sub>O<sub>3</sub>$  (71–5408) was detected in XRD analysis with a major peak at  $30.3^{\circ}$  (hkl;011) with an average crystallite size of 9.7 nm [\[35](#page-15-17)]. The NiO (PDF#44–1159) with major phase (101) was confirmed at  $37.5^{\circ}$  having an average crystallite size of 10.0 nm  $[32]$  $[32]$ . The major peak of NiAl<sub>2</sub>O<sub>4</sub> (PDF  $\text{\#10--0339}$  was detected at 37.09 $^{\circ}$  (311) with a crystallite size of 14.3 nm [[36\]](#page-15-18) and LaNiO<sub>3</sub> peak (PDF #33–0710) at 23.08° (100) while the crystallite size is 13.8 [\[37](#page-15-19)] with rhombohedral structure.

The reduction behaviour of the developed DRM catalyst was analysed using H<sub>2</sub>-TPR technique depicted in Fig. [2b](#page-4-0) for the La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> calcined at 700 °C. The TPR shows the first major peak at 552 °C with the H<sub>2</sub>-uptake of 249.3 µmol  $g^{-1}$  while the second major peak was detected at 695  $\degree$ C showing H<sub>2</sub>-uptake of 596.6 μmol g<sup>-1</sup>. The total H<sub>2</sub>-uptake of~850 μmol g<sup>-1</sup> which shows the 91% degree of reduction  $[38]$  $[38]$ . The higher H<sub>2</sub> uptake at elevated temperature shows the good interaction of  $Ni/La<sub>2</sub>O<sub>3</sub>$ -MgAl<sub>2</sub>O<sub>4</sub>. From the intense TPR peak at 695 °C, it is evident that NiO has been reduced into Ni  $[39]$  $[39]$ .

The basicity of  $MgAl<sub>2</sub>O<sub>4</sub>$  and  $Ni/La<sub>2</sub>O<sub>3</sub>MgAl<sub>2</sub>O<sub>4</sub>$  is investigated using CO<sub>2</sub>-TPD and presented in Fig. [3](#page-5-0) and Table [1.](#page-6-0) Three diferent peaks present at various regions from weak to strong basic nature of the prepared catalyst. The frst two peaks for MgAl<sub>2</sub>O<sub>4</sub> at 87 °C and 291 °C with CO<sub>2</sub> uptake of 347 µmol g<sup>-1</sup> and 122 µmol g<sup>-1</sup>, respectively, and indicating the weak basic sites [\[11](#page-14-10)]. While for Ni/  $La_2O_3MgAl_2O_4$ sample, the first two peaks were detected at 95  $^{\circ}$ C and 361  $^{\circ}$ C with CO<sub>2</sub> uptake of 206 μmol  $g^{-1}$  and 110 μmol  $g^{-1}$ , ascribed to the weak and medium basic sites, respectively. The distant peak shift from weak region to the medium is due to the addition of La<sub>2</sub>O<sub>3</sub>. The strong basic sites for MgAl<sub>2</sub>O<sub>4</sub> were detected at 542 <sup>o</sup>C



<span id="page-5-0"></span>**Fig. 3** CO<sub>2</sub> TPD analysis of La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> with inset CO<sub>2</sub> uptakes

<span id="page-6-0"></span>

having the CO<sub>2</sub> uptake of 463 µmol  $g^{-1}$  [[11\]](#page-14-10). In contrast, for Ni/La<sub>2</sub>O<sub>3</sub>.MgAl<sub>2</sub>O<sub>4</sub> sample, the strong basic sites were present at  $681\text{ °C}$  with the CO<sub>2</sub> uptake of 683  $\mu$ mol  $g^{-1}$ . The higher CO<sub>2</sub> uptake at the elevated temperature depicted the strong basic nature of the catalyst which is suitable for the DRM process and it is expected to exhibit better coke resistance during the long-term TOS tests [\[40](#page-15-22)].

The morphology of the prepared DRM catalysts was analysed by FESEM and depicted in Fig. [4.](#page-6-1) The MgAl<sub>2</sub>O<sub>4</sub> sample shows agglomerated porous structure pre-sented in Fig. [4](#page-6-1)a and  $La<sub>2</sub>O<sub>3</sub>$  shows a uniform web-like structure is evident in the



<span id="page-6-1"></span>**Fig.** 4 FESEM micrographs of **a** MgAl<sub>2</sub>O<sub>4</sub> **b** La<sub>2</sub>O<sub>3</sub> **c** La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> **d** TGA of La<sub>2</sub>O<sub>3</sub> co-supported  $Ni/MgAl<sub>2</sub>O<sub>4</sub>$ 

modifed preparation method using DMF as a surfactant which also assists in the uniform crystal growth (Fig. [4](#page-6-1)b). La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> sample resulted in a nanoflake-type structure depicted in Fig. [4](#page-6-1)c. The irregular structure of  $MgAl<sub>2</sub>O<sub>4</sub>$ is modified by web-like  $La_2O_3$  infusing with the Ni particles. Furthermore, the thermal stability of the  $La_2O_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> presented in Fig. [4d](#page-6-1). The total weight loss is less than  $3.5\%$  in the temperature range of 125 °C is ascribed to the removal of moisture [\[41](#page-15-23)].

The N<sub>2</sub> adsorption–desorption isotherms, surface area  $(S<sub>BFT</sub>)$ , average pore volume  $(V<sub>pore</sub>)$  and average pore radius is presented in Fig. [5](#page-7-0). The samples exhibited type IV isotherm confrming the formation of mesoporous structure material for all the synthesized samples. The surface area of  $MgAl<sub>2</sub>O<sub>4</sub>$  and  $La<sub>2</sub>O<sub>3</sub>$  was 102  $m^2$  g<sup>-1</sup>and 41.3 m<sup>2</sup> g<sup>-1</sup>, respectively. While the addition of Ni into La<sub>2</sub>O<sub>3</sub>-MgAl<sub>2</sub>O<sub>4</sub> reduces the surface area to 90  $m^2 g^{-1}$ . It is ascribed to the infusion of Ni particle on the surface of the catalyst support. The average pore radius of the MgAl<sub>2</sub>O<sub>4</sub>, La<sub>2</sub>O<sub>3</sub> and Ni/La<sub>2</sub>O<sub>3</sub>-MgAl<sub>2</sub>O<sub>4</sub> is 8.6 nm, 5.7 nm and 8.1 nm, respectively.

#### **Catalyst performance analysis**

The DRM activity test has been carried outing using the developed catalyst shown in Fig. [6.](#page-8-0) At frst, the DRM was carried without a catalyst which shows very low catalytic activity. The conversion of  $CH<sub>4</sub>$  and CO<sub>2</sub> is just below 10% at 700 °C. The selectivity of H<sub>2</sub> and CO is found to be less than 6%. In contrast, adding  $MgAl_2O_4$ catalyst in the fxed bed, the increment in the conversion and selectivity of the product is observed. The conversion of  $CH_4$  and  $CO_2$  is 35% and 32%, respectively. The selectivity H<sub>2</sub>, CO and C<sub>2</sub>H<sub>6</sub> is less than 12%, 15% and 3.5% respectively. The Ni impregnation in  $MgAl<sub>2</sub>O<sub>4</sub>$  further improves the catalytic activity with the increase



<span id="page-7-0"></span>**Fig. 5** N<sub>2</sub> adsorption–desorption of prepared samples with inset specific surface area (S<sub>BET</sub>) m<sup>2</sup> g<sup>-1</sup>, average pore volume ( $V_{pore}$ ) cm<sup>3</sup> g<sup>-1</sup> and average pore radius (nm)



<span id="page-8-0"></span>**Fig. 6** Catalysts performance evaluation: GHSV=1500  $h^{-1}$ , catalyst loading=0.3 g, feed ratio (CO<sub>2</sub>/  $CH<sub>4</sub>$ ) = 1, reaction temperature = 700 °C, reaction time = 2 h

in the conversion of CH<sub>4</sub> and CO<sub>2</sub> to 65 and 63%. Ni /MgAl<sub>2</sub>O<sub>4</sub> also substantially improves the selectivity of H<sub>2</sub>, CO and C<sub>2</sub>H<sub>6</sub> to 32%, 35% and 7.5% as depicted in Fig. [6](#page-8-0). Whereas, incorporating 20% La<sub>2</sub>O<sub>3</sub> as co-support into  $10\%$ Ni/MgAl<sub>2</sub>O<sub>4</sub> enhances the conversion of CH<sub>4</sub> and CO<sub>2</sub> to 87.3% and 89.5%, respectively. The selectivity of the H<sub>2</sub> improves from 32 to 51% for the composite  $La_2O_3$  co-supported  $Ni/MgAl<sub>2</sub>O<sub>4</sub>$  catalyst. CO selectivity is recorded 46% which is less than the selectivity of H<sub>2</sub>. In contrast,  $C_2H_6$  selectivity decrease to 4.5% in the La<sub>2</sub>O<sub>3</sub> co-supported  $Ni/MgAl<sub>2</sub>O<sub>4</sub>$ . This might be due to the higher yield and inhibition of methyl radical recombination [[23\]](#page-15-5).

The overall catalytic activity of the reported samples is in such order:  $MgAl_2O_4 < Ni/MgAl_2O_4 < La_2O_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub>. The non-co-supported catalyst activity is lower than that of Co-supported catalyst, which ascribes the occurrence of reverse water gas shift (RWGS) reaction is limited [\[23](#page-15-5)]. The  $La<sub>2</sub>O<sub>3</sub>$ co-supported catalyst resists the progress of RWGS and  $H<sub>2</sub>$  selectivity is improved. Furthermore, the possible formation of  $La_2O_2CO_3$  inhibit the carbon formation and improves the catalyst activity [\[23](#page-15-5)]. The improvement in the  $CH<sub>4</sub>$  conversion is due to the good formation of active sites as depicted in  $H_2$ -TPR results. The bulk formation of active sites activates CH<sub>4</sub> and resist the  $C_xH_x$  recombination by a further breakdown.

The comparison with the literature is drawn in Table [2](#page-9-0) for the reference. As we can see that the majority of the reports shows the  $H<sub>2</sub>/CO$  ratio below 1.0 except for Ni/h-BNNs catalyst reported by  $[42]$  $[42]$ . The higher H<sub>2</sub>/CO ratio depicts the CH<sub>4</sub> decomposition or Boudouard reaction. These reactions usually occur on Ni active



<span id="page-9-0"></span>

sites and block them, however, if  $\alpha$ -C is formed, it can be easily gasified or reacts with La<sub>2</sub>O<sub>3</sub> to form La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>[[23,](#page-15-5) [42\]](#page-15-24). The addition of La<sub>2</sub>O<sub>3</sub> also assists the chemisorption of  $CO<sub>2</sub>$  and regeneration of active metal and  $La<sub>2</sub>O<sub>3</sub>$  along with major sup-port MgAl<sub>2</sub>O<sub>4</sub> [[23,](#page-15-5) [24\]](#page-15-15).

#### **Catalyst stability and reaction mechanism**

The catalyst stability is one of the most important parameters after the fundamental catalytic performance. Herein, the  $La_2O_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> was tested for 20 h of time on stream (TOS) test keeping the process parameters constant. The conversion of CH<sub>4</sub> is shown in Fig. [7](#page-11-0)a, a stable trend having only 03% reduction in 20 h of TOS observed. Similarly,  $CO<sub>2</sub>$  also shows the same trend in the same TOS and experimental conditions. The stable conversion in the reported TOS for both reactants is encouraging for the reported catalyst. The selectivity of the  $H_2$  and CO partly declined during the 20 h TOS presented in Fig. [7](#page-11-0)b. The selectivity of the  $C_2H_6$  is slightly higher in the 20 h TOS. Figure [8](#page-12-0) shows that the H<sub>2</sub>/CO ratio is above unity during the 20 h TOS indicating the low carbon formation over the catalyst and enhanced stability.

The conversion stability of the developed catalyst is associated with better metalsupport interaction (MSI high active sites and high basicity due to the addition of  $La<sub>2</sub>O<sub>3</sub>$ . It also supports methane activation as well as  $CO<sub>2</sub>$  adsorption due to its basic nature [\[46](#page-15-28)]. The CH<sub>4</sub> activation is due to the Ni and formed Ni-C and 2H<sub>2</sub> (Eq. [10\)](#page-10-0). The formation of  $La_2O_2CO_3$  intermediate carbonate during the adsorption of  $CO_2$ (Eq. [11\)](#page-10-1) and after reaction with C-Ni to regenerate the  $La_2O_3$ , Ni and CO resist the carbon deposition on the catalyst surface (Eq. [12](#page-10-2)) [\[47](#page-15-29)]. The schematic representation of the reaction mechanism is proposed in Fig. [9](#page-12-1).

<span id="page-10-1"></span><span id="page-10-0"></span>
$$
CH_4 + Ni \rightarrow C - Ni + 2H_2 \tag{10}
$$

<span id="page-10-2"></span>
$$
CO2 + La2O3 \rightarrow La2O2CO3
$$
 (11)

$$
C - Ni + La2O2CO3 \rightarrow La2O3 + Ni + 2CO
$$
 (12)

#### **Characterization of the spent catalyst**

After 20 h of TOS, the spent catalyst has been characterized by EDX mapping and TGA. Figure [10a](#page-13-0) presented elemental mapping shows the formation of carbon over the surface of the catalyst. The mapping indicates the formation of carbon is not in the bulk form (Fig. [10](#page-13-0)b). The inset FESEM shows the formation of carbon nanofibres on the surface of the spent catalyst. The carbon nanofbres can easily reduce in the gasification process and formed CO or  $CO<sub>2</sub>$ .

The TGA profile of the spent  $La_2O_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> after 20 h of TOS shows the total weight loss of 9–10%, which confrms the formation of a lower amount



<span id="page-11-0"></span>**Fig. 7** Effect of time on stream **a** conversion of reactants  $(X_n)$  **b** H<sub>2</sub>, CO and C<sub>2</sub>H<sub>6</sub> selectivity  $(S_x)$  over La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub>; GHSV=1500 h<sup>-1</sup>, catalyst loading=0.3 g, feed ratio (CO<sub>2</sub>/CH<sub>4</sub>)=1, reaction temperature=700 °C

of carbon. The moisture and volatile matter removal are at 200  $^{\circ}$ C [\[11](#page-14-10), [48\]](#page-15-30) presented in Fig. [11.](#page-13-1) The weight loss in between 200–500 °C is associated with the fbrous carbon which is referred as β-carbon, as well as the decomposition of La-hydroxide intermediate phase which is usually formed under the moist conditions due to RWGS [\[29\]](#page-15-10). The total of 3% weight loss between 500–900 °C (Column III-IV) which confrm the low



<span id="page-12-0"></span>**Fig. 8** Time on stream vs H<sub>2</sub>/CO ratio over La<sub>2</sub>O<sub>3</sub> co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub>; GHSV = 1500 h<sup>-1</sup>, catalyst loading = 0.3 g, feed ratio (CO<sub>2</sub>/CH<sub>4</sub>) = 1, reaction temperature = 700 °C



<span id="page-12-1"></span>**Fig. 9** Proposed reaction mechanism for  $La_2O_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> based DRM

formation of carbon after 20 h TOS. This reduction is also ascribed to the dissociation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [[49](#page-15-31)]. The carbon formed above 700 °C is ascribed to filamentous carbon (γ-C).



<span id="page-13-0"></span>**Fig. 10 a** EDX mapping of spent catalyst **b** EDX elemental analysis with inset FEESEM



<span id="page-13-1"></span>**Fig. 11** TGA profile of spent  $\text{La}_2\text{O}_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> after 20 h TOS

### **Conclusions**

The synthesized  $La_2O_3$  co-supported Ni/MgAl<sub>2</sub>O<sub>4</sub> has been characterized using various techniques and employed for the DRM in thermal fxed bed reactor. The catalyst shows enhanced performance and higher  $H<sub>2</sub>/CO$  ratio, much suitable feedstock for downstream chemicals. The enhanced performance is ascribed to the suitable physicochemical properties of a catalyst such as metal-support interaction and the strong basic nature with well-structured morphology. While testing for longer runs, the catalyst shows stability for 20 h with less than 3% declined in the DRM activity and TGA of spent catalyst confrms the lower formation of carbon. This stability suggests the potential of the upgradation of the developed catalyst for the DRM process for industrial-scale production of syngas.

### **Authors Contibution**

Asif Hussain Khoja and Nor Aishah Saidina Amin develop the conceptualization of the work and drafted the manuscript. Arslan Mazhar assisted in material synthesis and in conducting the experiments. Mustafa Anwar and Sehar Shakir workout the material characterization analysis. Muhammad Taqi Mehran assisting in the result analysis of GC, drafting and revising the manuscript.

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