

Thermal dry reforming of methane over La₂O₃ co-supported Ni/MgAl₂O₄ catalyst for hydrogen-rich syngas production

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Abstract

The excess emission of greenhouse gases (GHGs) such as CO₂ and CH₄ is posing an acute threat to the environment, and efficient ways are being sought to utilize GHGs to produce syngas (H₂, CO) and lighter hydrocarbons (HCs). In this study, the dry reforming of methane (DRM) has been carried out at 700 °C using La₂O₃ co-supported Ni/MgAl₂O₄ nano-catalyst in a fixed bed thermal reactor. The catalyst is characterized using various techniques such as XRD, FESEM, EDX-mapping, CO₂-TPD, H₂-TPR and TGA. The modified MgAl₂O₄ shows the flake type structure after the addition of La_2O_3 . The TPR and TPD analysis shows the highly dispersed metal and strong basic nature of the catalyst consequently enhances the conversion of CO₂ and CH₄. The highest conversion for CH₄ is 87.3% while CO₂ conversion is nearly 89.5% in 20 h of operation time. The selectivity of H₂ and CO approached 50% making the H₂/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 MgAl₂O₄ \cdot H₂ production \cdot syngas

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Introduction

Dry reforming of methane (DRM) (Eq. 1) is an important technique which has been used to convert the greenhouse gases such as CO_2 and CH_4 to syngas (H_2 , CO) and lighter hydrocarbons (C_2 - C_3) [1]. The syngas can be used as feedstock for the wellknown Fischer–Tropsch (FT) synthesis process in gas-to-liquid fuel technology [2]. The CH_4 and CO_2 have been successfully converted into fuels via DRM [3], however, the carbon deposition is a major concern identified in the recent studies [4, 5]. Mainly, the carbon is formed via two famous reactions which are methane cracking (Eq. 2) and Boudouard reaction (Eq. 3) [6]. Another issue is the H_2/CO ratio, which is usually less than unity due to the reverse water gas shift reaction (RWGS) (Eq. 4) [7, 8].

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

$$CH_4 \rightarrow C + H_2 \Delta H^\circ = 75 \text{kJ mol}^{-1} \text{ (Methane cracking)}$$
 (2)

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

$$CO_2 + H_2 \rightarrow CO + H_2O \Delta H^\circ = 41.27 \text{ kJ mol}^{-1} \text{ (RWGS)}$$
(4)

The aim of developing an efficient and stable catalyst is to improve the conversion efficiency, stability and H_2/CO ratio with lower carbon formation [9]. Various catalyst systems were employed to improve the conversion efficiency. The Nibased catalyst with various supports such as Al_2O_3 [10], $MgAl_2O_4$ [11], SiO_2 [12], Mesoporous silica molecular sieves (MCM) [13], MgO [14], zeolites [15] and ZrO_2 [16] were reported for DRM [17]. Furthermore, co-supported catalysts were also extensively studied with multiple objectives such as CO_2 adsorption and metal dispersion [14, 18]. 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].

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 Al_2O_3 -MgO [20]. To achieve the communal effect of both Al and Mg, the Ni/MgAl₂O₄ spinel has been synthesized for DRM, and it resulted in a stable and enhanced performance than Ni/Al₂O₃. However, issues such as carbon formation and H₂/CO ratio were not resolved [21, 22]. The catalyst performance in the DRM also depends on the physicochemical properties of the material. The physicochemical properties of catalyst can be modified by the preparation techniques and by introducing a co-support which will improve the basicity and metal dispersion on the catalyst support [23–25]. The basic nature of the catalyst is also important for carbon deposition and deactivation of the catalytic performance [26, 27]. Ni interface with MgAl₂O₄ is improved by the communal effect of MgAl₂O₄ and La_2O_3 as mixed matrix support [28]. In thermo-catalytic DRM, the combined effect of La_2O_3 and $MgAl_2O_4$ catalyst is barely reported [29].

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/La₂O₃-MgAl₂O₄ and tested for DRM in a fixed bed thermal reactor. The catalyst material was characterized by X-ray diffraction (XRD), field emission electron microscopy (FESEM), H₂ temperature-programmed reduction (H₂-TPR), CO₂ temperature-programmed desorption (CO₂-TPD), N₂ 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

 $MgAl_2O_4$ and La_2O_3 spinal was prepared by modifying the co-precipitation method followed by hydrothermal process reported elsewhere [30]. For MgAl₂O₄ 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 La₂O₃. For co-support, $MgAl_2O_4$ and La_2O_3 were taken as 4:1 (wt. ratio) as co-support and prepared by microemulsion technique [31]. The 10% wt. Ni as the active metal was impregnated by the modified incipient wetness impregnation method [32]. The catalyst was then calcined at 700 °C for 3 h in a muffle furnace. The material was characterized by XRD, FESEM, H₂-TPR, CO₂-TPD, EDX-mapping, BET and TGA. The characterization methods and equipment details were reported elsewhere [32]. The crystallography and morphology of the catalyst were analysed by XRD, FESEM and BET. The crystallite size was calculated using the Scherrer equation [32, 33]. 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 fixed-bed thermal reactor is presented in Fig. 1. Briefly, the feed gases CH_4 (99.99%) and CO_2 (99.99%) controlled by a mass flow controller (ALICAT) were provided to the fixed bed reactor. The fixed-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



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 flame ionization detector (FID) [29].

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. (5-9). When *n* represents the number of moles of the individual species. The experiments were repeated twice to determine the relative error.

$$CH_{4} \text{ conversion } (X_{CH_{4}})\% = \left[\frac{(nCH_{4})_{\text{converted}}}{(nCH_{4})_{\text{feed}}} \times 100\right]$$
(5)

$$CO_{2} \text{ conversion } (X_{CO_{2}})\% = \left[\frac{(n CO_{2})_{\text{converted}}}{(n CO_{2})_{\text{feed}}} \times 100\right]$$
(6)

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

$$H_2 \text{ selectivity } (S_{H_2})\% = \left[\frac{(nH_2)_{\text{produced}}}{(2 \times nCH_4)_{\text{converted}}} \times 100\right]$$
(8)

$$C_2 H_6 \text{ selectivity } (S_{C_2 H_6})\% = \left[\frac{(2 \times nC_2 H_6)_{\text{produced}}}{(nCH_4 + nCO_2)_{\text{converted}}} \times 100\right]$$
(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. 2a. The X-ray diffraction peaks for $MgAl_2O_4$



Fig. 2 a XRD of the prepared samples b H₂-TPR with inset H₂ uptake profile and

(PDF#72–6947) were analysed, and the cubical phase (hkl; 311) was confirmed at 38.5° with a space group of 227: Fd3m [24, 34]. The average crystallite size for MgAl₂O₄ was 10.5 nm. Similarly, La₂O₃ (71–5408) was detected in XRD analysis with a major peak at 30.3° (hkl;011) with an average crystallite size of 9.7 nm [35]. The NiO (PDF#44–1159) with major phase (101) was confirmed at 37.5° having an average crystallite size of 10.0 nm [32]. The major peak of NiAl₂O₄ (PDF #10–0339) was detected at 37.09° (311) with a crystallite size of 14.3 nm [36] and LaNiO₃ peak (PDF #33–0710) at 23.08° (100) while the crystallite size is 13.8 [37] with rhombohedral structure.

The reduction behaviour of the developed DRM catalyst was analysed using H₂-TPR technique depicted in Fig. 2b for the La₂O₃ co-supported Ni/MgAl₂O₄ calcined at 700 °C. The TPR shows the first major peak at 552 °C with the H₂-uptake of 249.3 µmol g⁻¹ while the second major peak was detected at 695 °C showing H₂-uptake of 596.6 µmol g⁻¹. The total H₂-uptake of ~850 µmol g⁻¹ which shows the 91% degree of reduction [38]. The higher H₂ uptake at elevated temperature shows the good interaction of Ni/La₂O₃-MgAl₂O₄.From the intense TPR peak at 695 °C, it is evident that NiO has been reduced into Ni [39].

The basicity of MgAl₂O₄ and Ni/La₂O₃.MgAl₂O₄ is investigated using CO₂-TPD and presented in Fig. 3 and Table 1. Three different peaks present at various regions from weak to strong basic nature of the prepared catalyst. The first two peaks for MgAl₂O₄ at 87 °C and 291 °C with CO₂ uptake of 347 µmol g⁻¹ and 122 µmol g⁻¹, respectively, and indicating the weak basic sites [11]. While for Ni/La₂O₃.MgAl₂O₄ sample, the first two peaks were detected at 95 °C and 361 °C with CO₂ 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 La₂O₃. The strong basic sites for MgAl₂O₄ were detected at 542 °C



Fig. 3 CO2 TPD analysis of La2O3 co-supported Ni/MgAl2O4 and MgAl2O4 with inset CO2 uptakes

Table 1 CO2 uptake for MgAl2O4 and 10% Ni/La2O3- MgAl2O4 MgAl2O4	Peak #	Sample	Temperature (°C)	CO_2 uptake (μ mol g ⁻¹)
	1	$MgAl_2O_4$	80	347
		10% Ni/La ₂ O ₃ -MgAl ₂ O ₄	85	206
	2	$MgAl_2O_4$	291	121
		10% Ni/La ₂ O ₃ -MgAl ₂ O ₄	301	110
	3	$MgAl_2O_4$	542	462
		10% Ni/La ₂ O ₃ -MgAl ₂ O ₄	681	683

having the CO_2 uptake of 463 µmol g⁻¹ [11]. In contrast, for Ni/La₂O₃.MgAl₂O₄ sample, the strong basic sites were present at 681 °C with the CO₂ uptake of 683 µmol g⁻¹. The higher CO₂ 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].

The morphology of the prepared DRM catalysts was analysed by FESEM and depicted in Fig. 4. The $MgAl_2O_4$ sample shows agglomerated porous structure presented in Fig. 4a and La_2O_3 shows a uniform web-like structure is evident in the



Fig. 4 FESEM micrographs of a MgAl₂O₄ b La₂O₃ c La₂O₃ co-supported Ni/MgAl₂O₄ d TGA of La₂O₃ co-supported Ni/MgAl₂O₄

modified preparation method using DMF as a surfactant which also assists in the uniform crystal growth (Fig. 4b). La_2O_3 co-supported Ni/MgAl₂O₄ sample resulted in a nanoflake-type structure depicted in Fig. 4c. The irregular structure of MgAl₂O₄ 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/MgAl₂O₄ presented in Fig. 4d. The total weight loss is less than 3.5% in the temperature range of 125 °C is ascribed to the removal of moisture [41].

The N₂ adsorption–desorption isotherms, surface area (S_{BET}), average pore volume (V_{pore}) and average pore radius is presented in Fig. 5. The samples exhibited type IV isotherm confirming the formation of mesoporous structure material for all the synthesized samples. The surface area of MgAl₂O₄ and La₂O₃ was 102 m² g⁻¹ and 41.3 m² g⁻¹, respectively. While the addition of Ni into La₂O₃-MgAl₂O₄ reduces the surface area to 90 m² g⁻¹. It is ascribed to the infusion of Ni particle on the surface of the catalyst support. The average pore radius of the MgAl₂O₄, La₂O₃ and Ni/La₂O₃-MgAl₂O₄ 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. At first, the DRM was carried without a catalyst which shows very low catalytic activity. The conversion of CH_4 and CO_2 is just below 10% at 700 °C. The selectivity of H_2 and CO is found to be less than 6%. In contrast, adding MgAl₂O₄ catalyst in the fixed 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_2 , CO and C_2H_6 is less than 12%, 15% and 3.5% respectively. The Ni impregnation in MgAl₂O₄ further improves the catalytic activity with the increase



Fig. 5 N₂ adsorption–desorption of prepared samples with inset specific surface area (S_{BET}) m² g⁻¹, average pore volume (V_{pore}) cm³ g⁻¹ and average pore radius (nm)



Fig. 6 Catalysts performance evaluation: $GHSV = 1500 h^{-1}$, catalyst loading = 0.3 g, feed ratio (CO_2/CH_4) = 1, reaction temperature = 700 °C, reaction time = 2 h

in the conversion of CH₄ and CO₂ to 65 and 63%. Ni /MgAl₂O₄ also substantially improves the selectivity of H₂, CO and C₂H₆ to 32%, 35% and 7.5% as depicted in Fig. 6. Whereas, incorporating 20% La₂O₃ as co-support into 10%Ni/MgAl₂O₄ enhances the conversion of CH₄ and CO₂ to 87.3% and 89.5%, respectively. The selectivity of the H₂ improves from 32 to 51% for the composite La₂O₃ co-supported Ni/MgAl₂O₄ catalyst. CO selectivity is recorded 46% which is less than the selectivity of H₂. In contrast, C₂H₆ selectivity decrease to 4.5% in the La₂O₃ co-supported Ni/MgAl₂O₄. This might be due to the higher yield and inhibition of methyl radical recombination [23].

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_2O_4. 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]. The La_2O_3 co-supported catalyst resists the progress of RWGS and H₂ selectivity is improved. Furthermore, the possible formation of La₂O₂CO₃ inhibit the carbon formation and improves the catalyst activity [23]. The improvement in the CH₄ conversion is due to the good formation of active sites as depicted in H₂-TPR results. The bulk formation of active sites activates CH₄ and resist the C_xH_x recombination by a further breakdown.

The comparison with the literature is drawn in Table 2 for the reference. As we can see that the majority of the reports shows the H_2/CO ratio below 1.0 except for Ni/h-BNNs catalyst reported by [42]. The higher H_2/CO ratio depicts the CH₄ decomposition or Boudouard reaction. These reactions usually occur on Ni active

Catalyst	Parameters	${ m X}_{{ m CH}_4}$ (%)	X _{CO2} (%)	H_2/CO ratio	Ref
Pt/CePr/Al2O3	$CH_4:CO_2 = 1, 100 \text{ ml min}^{-1}$	69	77	6.0	[43]
Ni/Sn0.02/A1	100 ml min^{-1} , CH ₄ :CO ₂ = 1, WHSV, 60,000 ml g ⁻¹ cat h ⁻¹	42	78	0.9	[44]
Ni/Al	100 ml min^{-1} , CH ₄ :CO ₂ = 1, WHSV, 60,000 ml g ⁻¹ cat h ⁻¹ 700 °C	49	76	0.8	[44]
Ni/h-BNNs	100 ml min^{-1} , CH ₄ :CO ₂ = 1, WHSV, 35,000 ml g ⁻¹ cat h ⁻¹	06	70	1.05	[42]
Ni/La ₂ O ₃ -LOC	$CH_4:CO_2 = 1$, WHSV = 60,000 mL h ⁻¹ gcat ⁻¹ , 700 °C	78	81	0.89	[23]
$Ni_{0.07}Mg_{0.93}O-R$	$CH_4:CO_2 = 1$, WHSV = 86,000 mL h ⁻¹ gcat ⁻¹ , 800 °C	82	88	0.9	[45]
Ni/La ₂ O ₃ -Al ₂ O ₃	$CH_4:CO_2 = 1$, GHSV = 60 mL gcat ⁻¹ , 700 °C	82.4	77.3	0.95	[24]
Ni/La ₂ O ₃ -MgAl ₂ O ₄	$CH_4:CO_2 = 1$, $GHSV = 15,000 h^{-1}$, 700 °C	87.3	89.5	1.1	This work

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sites and block them, however, if α -C is formed, it can be easily gasified or reacts with La₂O₃ to form La₂O₂CO₃[23, 42]. The addition of La₂O₃ also assists the chemisorption of CO₂ and regeneration of active metal and La₂O₃ along with major support MgAl₂O₄ [23, 24].

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/MgAl₂O₄ was tested for 20 h of time on stream (TOS) test keeping the process parameters constant. The conversion of CH₄ is shown in Fig. 7a, a stable trend having only 03% reduction in 20 h of TOS observed. Similarly, CO₂ 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 H₂ and CO partly declined during the 20 h TOS presented in Fig. 7b. The selectivity of the C₂H₆ is slightly higher in the 20 h TOS. Figure 8 shows that the H₂/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_2O_3 . It also supports methane activation as well as CO_2 adsorption due to its basic nature [46]. The CH_4 activation is due to the Ni and formed Ni-C and $2H_2$ (Eq. 10). The formation of $La_2O_2CO_3$ intermediate carbonate during the adsorption of CO_2 (Eq. 11) 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) [47]. The schematic representation of the reaction mechanism is proposed in Fig. 9.

$$CH_4 + Ni \rightarrow C - Ni + 2H_2 \tag{10}$$

$$\mathrm{CO}_2 + \mathrm{La}_2\mathrm{O}_3 \to \mathrm{La}_2\mathrm{O}_2\mathrm{CO}_3 \tag{11}$$

$$C - Ni + La_2O_2CO_3 \rightarrow La_2O_3 + Ni + 2CO$$
(12)

Characterization of the spent catalyst

After 20 h of TOS, the spent catalyst has been characterized by EDX mapping and TGA. Figure 10a 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. 10b). The inset FESEM shows the formation of carbon nanofibres on the surface of the spent catalyst. The carbon nanofibres can easily reduce in the gasification process and formed CO or CO_2 .

The TGA profile of the spent La_2O_3 co-supported Ni/MgAl₂O₄ after 20 h of TOS shows the total weight loss of 9–10%, which confirms the formation of a lower amount



Fig. 7 Effect of time on stream **a** conversion of reactants (X_n) **b** H_2 , CO and C_2H_6 selectivity (S_x) over La₂O₃ co-supported Ni/MgAl₂O₄; GHSV=1500 h⁻¹, catalyst loading=0.3 g, feed ratio $(CO_2/CH_4)=1$, reaction temperature=700 °C

of carbon. The moisture and volatile matter removal are at 200 °C [11, 48] presented in Fig. 11. The weight loss in between 200–500 °C is associated with the fibrous 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]. The total of 3% weight loss between 500–900 °C (Column III-IV) which confirm the low



Fig. 8 Time on stream vs H_2 /CO ratio over La₂O₃ co-supported Ni/MgAl₂O₄; GHSV = 1500 h⁻¹, catalyst loading = 0.3 g, feed ratio (CO₂/CH₄) = 1, reaction temperature = 700 °C



Fig. 9 Proposed reaction mechanism for La2O3 co-supported Ni/MgAl2O4 based DRM

formation of carbon after 20 h TOS. This reduction is also ascribed to the dissociation of $La_2O_2CO_3$ [49]. The carbon formed above 700 °C is ascribed to filamentous carbon (γ -C).



Fig. 10 $\,$ a EDX mapping of spent catalyst b EDX elemental analysis with inset FEESEM



Fig. 11 TGA profile of spent La_2O_3 co-supported Ni/MgAl₂O₄ after 20 h TOS

Conclusions

The synthesized La₂O₃ co-supported Ni/MgAl₂O₄ has been characterized using various techniques and employed for the DRM in thermal fixed bed reactor. The catalyst shows enhanced performance and higher H₂/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 confirms 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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References

- 1. J.A. Frankel, Greenhouse Gas Emissions (Brookings Institution, Washington, D.C, 1999)
- 2. A. Rafiee, K. Rajab Khalilpour, D. Milani, M. Panahi, J. Environ. Chem. Eng. 6(5), (2018)
- 3. R. Dębek, K. Zubek, M. Motak, P. Da Costa, T. Grzybek, Res. Chem. Intermed. 41(12), (2015)
- 4. A.H. Khoja, M. Tahir, N.A.S. Amin, Energy Convers. Manag. 183, (2019)
- M.A. Gerber, Review of Novel Catalysts for Biomass Tar Cracking and Methane Reforming (Pacific Northwest National Laboratory Richland, WA, USA, 2007)
- 6. Y.H. Hu, E. Ruckenstein, Adv. Catal. 48(49), (2004)
- 7. B. Abdullah, N.A.A. Ghani, D.V.N. Vo, J. Clean. Prod. 162, (2017)
- 8. E. Horvath, K. Baan, E. Varga, A. Oszko, A. Vago, M. Toro, A. Erdohelyi, Catal. Today 281, (2017)
- 9. M. Usman, W.M.A.W. Daud, H.F. Abbas, Renew. Sustain. Energy Rev. 45, (2015)
- K. Selvarajah, N.H.H. Phuc, B. Abdullah, F. Alenazey, D.-V.N. Vo, Res. Chem. Intermed. 42(1), (2016)
- 11. I.H. Son, S. Kwon, J.H. Park, S.J. Lee, Nano Energy 19, Supplement C (2016)
- 12. S. Tomiyama, R. Takahashi, S. Sato, T. Sodesawa, S. Yoshida, Appl. Catal. A Gen. 241(1-2), (2003)
- 13. H. Arbag, S. Yasyerli, N. Yasyerli, G. Dogu, Int. J. Hydrog. Energy 35(6), (2010)
- 14. Y.J.O. Asencios, E.M. Assaf, Fuel Process. Technol. 106, (2013)
- P. Frontera, A. Aloise, A. Macario, F. Crea, P.L. Antonucci, G. Giordano, J.B. Nagy, Res. Chem. Intermed. 37(2), (2011)
- 16. N. Rahemi, M. Haghighi, A.A. Babaluo, M.F. Jafari, P. Estifaee, J. Ind. Eng. Chem. 19(5), (2013)
- V. Sadykov, V. Rogov, E. Ermakova, D. Arendarsky, N. Mezentseva, G. Alikina, N. Sazonova, A. Bobin, S. Pavlova, Y. Schuurman C. Mirodatos, Thermochim. Acta 567, (2013)

- 18. S.H. Zeng, L. Zhang, X.H. Zhang, Y. Wang, H. Pan, H.Q. Su, Int. J. Hydrog. Energy 37(13), (2012)
- 19. D. Pakhare, J. Spivey, Chem. Soc. Rev. 43(22), (2014)
- 20. L. Zhang, Q. Zhang, Y. Liu, Y. Zhang, Appl. Surf. Sci. 389, Supplement C (2016)
- 21. S. Dash, R.K. Sahoo, A. Das, S. Bajpai, D. Debasish, S.K. Singh, J. Alloys Compd. 726, Supplement C (2017)
- 22. H.-J. Kim, E.-H. Yang, Y.S. Noh, G.H. Hong, J.I. Park, S.A. Shin, K.-Y. Lee, D.J. Moon, Res. Chem. Intermed. 44(2), (2017)
- 23. X.Y. Li, D. Li, H. Tian, L. Zeng, Z.J. Zhao, J.L. Gong, Appl. Catal. B-Environ. 202, (2017)
- 24. A.S. Al-Fatesh, M.A. Naeem, A.H. Fakeeha, A.E. Abasaeed, Chin. J. Chem. Eng. 22(1), (2014)
- 25. M.A. Uzair, A. Waqas, A.H. Khoja, N. Ahmed, Energy Source Part A 38(24), (2016)
- 26. A.H. Khoja, M. Tahir, N.A.S. Amin, A. Javed, M.T. Mehran, Int. J. Hydrog. Energy 45(22), (2020)
- 27. R. Pereñiguez, V.M. Gonzalez-delaCruz, A. Caballero, J.P. Holgado, Appl. Catal. B: Environ. 123, (2012)
- 28. D.X. Li, P. Pirouz, A.H. Heuer, S. Yadavalli, C.P. Flynn, Philos. Mag. A 65(2), (1992)
- 29. A.H. Khoja, M. Tahir, N.A.S. Amin, Energy Convers. Manag. 144, (2017)
- A. Samad, K.Y. Lau, I.A. Khan, A.H. Khoja, M.M. Jaffar, M. Tahir, J. Phys. Chem. Solids 120, (2018)
- 31. M. Usman, W.M.A.W. Daud, RSC Adv. 6(44), (2016)
- 32. A.H. Khoja, M. Tahir, N.A.S. Amin, Fuel Process. Technol. 178, (2018)
- 33. A.H. Khoja, M. Tahir, N.A. Saidina Amin, Energy Fuels 33(11), (2019)
- 34. S. Sokolov, E.V. Kondratenko, M.M. Pohl, A. Barkschat, U. Rodemerck, Appl. Catal. B-Environ. 113, (2012)
- 35. D. Ağaoğulları, İ. Duman, M.L. Öveçoğlu, Ceramics Int. 38(8), (2012)
- 36. N. Sahli, C. Petit, A.C. Roger, A. Kiennemann, S. Libs, M.M. Bettahar, Catal. Today 113(3), (2006)
- 37. X. Song, X. Dong, S. Yin, M. Wang, M. Li, H. Wang, Appl. Catal. A Gen. 526, (2016)
- A. Bordoloi, S. Das, R. Goyal, R.K. Singha, C.R. Pendem, S.K.L. Narayan, R. Bal, V.V.D.N. Prasad, N.N. Botcha, M. Kumar, (Google Patents, 2017)
- 39. J. Shen, A.A.C. Reule, N. Semagina, Int. J. Hydrog. Energy 44(10), (2019)
- 40. S. Das, M. Sengupta, J. Patel, A. Bordoloi, Appl. Catal. a-Gen. 545, Supplement C (2017)
- 41. J. Guo, H. Lou, H. Zhao, X. Zheng, React. Kinet. Catal. Lett. 84(1), (2005)
- 42. Y. Cao, P. Maitarad, M. Gao, T. Taketsugu, H.R. Li, T.T. Yan, L.Y. Shi, D.S. Zhang, Appl. Catal. B-Environ. 238, (2018)
- R.O. da Fonseca, R.C. Rabelo-Neto, R.C.C. Simões, L.V. Mattos, F.B. Noronha, Int. J. Hydrog. Energy 45(8), (2020)
- 44. U. Guharoy, E. Le Sache, Q. Cai, T.R. Reina, S. Gu, J. CO₂ Util. 27, (2018)
- 45. T. Zhang, Z. Liu, Y.-A. Zhu, Z. Liu, Z. Sui, K. Zhu, X. Zhou, Appl. Catal. B: Environ. 264, (2020)
- 46. L. Zhang, X. Wang, C. Chen, X. Zou, X. Shang, W. Ding, X. Lu, RSC Adv. 7(53), (2017)
- 47. J.K. Xu, W. Zhou, J.H. Wang, Z.J. Li, J.X. Ma, Chin. J. Catal. 30(11), (2009)
- C.C. Chong, Y.W. Cheng, H.D. Setiabudi, N. Ainirazali, D.-V.N. Vo, B. Abdullah, Int. J. Hydrog. Energy 45(15), (2020)
- 49. E.P. Komarala, I. Komissarov, B.A. Rosen, Catalysts 10(1), (2019)

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