Article

Performance Analysis of TiO_2-Modified Co/MgAl_2O_4 Catalyst for Dry Reforming of Methane in a Fixed Bed Reactor for Syngas (H_2, CO) Production

Arslan Mazhar 1, Asif Hussain Khoja 1,*#, Abul Kalam Azad 2,*#, Faisal Mushtaq 3, Salman Raza Naqvi 4,*#; Sehar Shakir 5, Muhammad Hassan 5,*#; Rabia Liaquat 5 and Mustafa Anwar 5,*#

1 Fossil Fuels Laboratory, Department of Thermal Energy Engineering, U.S.-Pakistan Centre for Advanced Studies in Energy (USPCAS-E), National University of Sciences & Technology (NUST), Sector H-12, Islamabad 44000, Pakistan; arslanmazhar52@gmail.com
2 School of Engineering and Technology, Central Queensland University, 120 Spencer Street, Melbourne, VIC 3000, Australia
3 Department of Chemical Engineering, Faculty of Engineering & Architecture, Balochistan University of Information Technology, Engineering and Management Sciences, Airport Road, Baily, Quetta 87300, Pakistan; faisalqta1977@gmail.com
4 School of Chemical and Materials Engineering (SCME), National University of Sciences & Technology (NUST), Sector H-12, Islamabad 44000, Pakistan; salman.raza@scme.nust.edu.pk
5 Department of Energy Systems Engineering, U.S.-Pakistan Centre for Advanced Studies in Energy (USPCAS-E), National University of Sciences & Technology (NUST), Sector H-12, Islamabad 44000, Pakistan; sehar@uspcase.nust.edu.pk (S.S.); hassan@uspcase.nust.edu.pk (M.H.); rabia@uspcase.nust.edu.pk (R.L.); mustafa@uspcase.nust.edu.pk (M.A.)
* Correspondence: asif@uspcase.nust.edu.pk (A.H.K.); a.k.azad@cqu.edu.au (A.K.A.)

Abstract: Co/TiO_2–MgAl_2O_4 was investigated in a fixed bed reactor for the dry reforming of methane (DRM) process. Co/TiO_2–MgAl_2O_4 was prepared by modified co-precipitation, followed by the hydrothermal method. The active metal Co was loaded via the wetness impregnation method. The prepared catalyst was characterized by XRD, SEM, TGA, and FTIR. The performance of Co/TiO_2–MgAl_2O_4 for the DRM process was investigated in a reactor with a temperature of 750 °C, a feed ratio (CO_2/CH_4) of 1, a catalyst loading of 0.5 g, and a feed flow rate of 20 mL min^{-1}. The effect of support interaction with metal and the composite were studied for catalytic activity, the composite showing significantly improved results. Moreover, among the tested Co loadings, 5 wt% Co over the TiO_2–MgAl_2O_4 composite shows the best catalytic performance. The 5%Co/TiO_2–MgAl_2O_4 improved the CH_4 and CO_2 conversion by up to 70% and 80%, respectively, while the selectivity of H_2 and CO improved to 43% and 46.5%, respectively. The achieved H_2/CO ratio of 0.9 was due to the excess amount of CO produced because of the higher conversion rate of CO_2 and the surface carbon reaction with oxygen species. Furthermore, in a time on stream (TOS) test, the catalyst exhibited 75 h of stability with significant catalytic activity. Catalyst potential lies in catalyst stability and performance results, thus encouraging the further investigation and use of the catalyst for the long-run DRM process.

Keywords: dry reforming of methane; TiO_2; MgAl_2O_4; syngas; hydrothermal process

1. Introduction

The rising concerns over greenhouse gas (GHG) emissions on global warming and climate change has motivated many industrial production facilities to reconsider plans on how to effectively control and recycle GHGs to produce synthetic fuels [1,2]. Synthesis gas (mainly made of H_2 and CO) is a vital fuel gas mixture currently being employed as an alternative to petroleum-based fuels. Syngas is considered the primary feedstock in the production of some important liquid fuels, such as ammonia and methanol, and it can also
be used as an intermediate resource to produce H₂, synthetic petroleum, and hydrocarbon products [3–5].

Syngas can be produced from various routes and techniques. The catalytic reforming technologies for syngas production, such as the steam reforming of methane (SRM) [6], partial oxidation of methane (POM) [5], and dry reforming of methane (DRM) [7,8], have gained much importance in recent years [9,10]. The DRM has been shown to be a promising technique that employs two major GHGs (CH₄ and CO₂) as feedstock to produce syngas [11,12]. The H₂/CO syngas ratio produced above unity as a result of the DRM reaction is favourable for the synthesis of value-added chemicals and long-chain hydrocarbons for Fischer–Tropsch (FT) synthesis [13]. The DRM converts stable molecules of CO₂ and CH₄ via catalytic pathways into syngas when mixed in unit proportion (Equation (1)).

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2 \quad \Delta H^{\circ}_{25^\circ C} = 247 \text{ kJ mol}^{-1} \quad \text{(DRM)}
\]  

The DRM has some notable disadvantages, as it promotes reverse water-gas shift reaction (RWGS) and carbon formation via methane decomposition [14,15]. RWGS mainly occurs when the H₂ to CO ratio becomes less than unity. The carbon formation is expressed by the famous Boudouard reaction, which can result in the deactivation of catalysts [16,17] Equations (2) and (3).

\[
\text{CH}_4 \rightarrow \text{C} + \text{H}_2 \quad \Delta H^{\circ}_{25^\circ C} = 75 \text{ kJ mol}^{-1} \quad \text{(Methane cracking)}
\]

\[
2 \text{CO} \rightarrow \text{C} + \text{CO}_2 \quad \Delta H^{\circ}_{25^\circ C} = -172 \text{ kJ mol}^{-1} \quad \text{(Boudouard reaction)}
\]

It is understood that carbon formation has adverse effects on the reaction mechanism and results in carbon deposition, thus leading to the deactivation of catalysts that affect the reaction lifetime and altering the H₂/CO ratio [18,19]. To have a better understanding of coke formation, understanding the thermodynamics of the DRM is important for commercial DRM process implementation. Thus, the development of a catalyst with a high catalytic performance and resistance to coking is an important objective [20]. In this regard, catalyst performance depends on active metal and support properties, their interaction, and their catalytic behaviour.

In the catalytic DRM, noble metals like rhodium (Rh), palladium (Pd), and ruthenium (Ru) are recognised as stable catalysts that can inhibit carbon formation but are commercially unviable [21–23]. Nickel (Ni) is the most widely used commercially active metal due to its availability and good catalytic activity. The carbon deposition rate and sintering of the Ni catalyst still need to be addressed in the DRM [24–26]. Cobalt (Co) exhibits a better stability to carbon deposition, but its performance in the DRM must be improved [27–30]. For instance, El et al. [31] investigated the effects of confinement on the catalytic performance of two silica supports (SiO₂ and SBA-15) on Co loading. The results indicated that Co/SBA-15 showed stability against the sintering of mesopores during the DRM and that the addition of rhodium to Co/SBA-15 led to increased stability and activity with less carbon coking.

The effect of the support on the catalyst depends on the nature of the support, which can play an essential role in the activity and stability of the catalyst [32]. MgAl₂O₄ is an excellent support material with a high sintering resistance, good hydrothermal stability, and excellent mechanical strength [3,14,33]. During the DRM, CO₂ dissociation and adsorption proceed at a faster rate with the use of basic support, and, in this regard, MgAl₂O₄ can be used as a support material due to its basic nature and high surface area [34–36]. DRMs done using different Ni loadings on nanocrystalline MgAl₂O₄ (with its high surface area) have shown high catalytic activity and stability, with an increase in carbon deposition following the increase in Ni loading [14,37].

Bi-support catalysts can be very effective in improving mechanical properties and catalytic performance. For example, TiO₂ provided some favourable properties for the DRM [38]. The strong metal–support interaction between the TiO₂ support and metal exhibited a high resistance towards coke deposition while increasing catalyst activity and
stability. The activity and stability of TiO₂ can be improved using a structured TiO₂-based catalyst [38,39]. In catalysis, a higher catalytic activity has been observed with the use of metal supported on TiO₂ nanowires. The use of a low-temperature SRM using Ni/TiO₂ as a catalyst revealed that stronger metal–support interactions assisted low-temperature methane activation while Ni species aided in hydrogen production via WGSR. It was reported that Ni/TiO₂ showed an enhanced coking resistance [40]. Though TiO₂ nanowires have been investigated for other photocatalytic and fuel cell applications, their effect on the DRM with a combination of the Co transition metal and added bi-support has yet to be investigated [41]. The combination of TiO₂ and MgAl₂O₄ as co-supports and Co as an active metal could enhance the CH₄ and CO₂ activation, resist carbon formation, and aid stability.

In this study, the catalytic performance of a TiO₂ nanowire-modified Co/MgAl₂O₄ catalyst was investigated for the DRM in a fixed bed reactor. Co/TiO₂–MgAl₂O₄ was synthesised by the co-precipitation process, the hydrothermal method, and the wetness impregnation method. The catalyst was characterised using various techniques such as XRD, SEM, EDS, TGA, and FTIR. The catalyst was tested for the DRM activity and the effect of metal loading, and stability tests were conducted for longer times on stream (TOS). Furthermore, the spent catalyst was characterised by XRD, SEM-EDS, and TGA to analyse the carbon formation during the TOS and to present a possible reaction mechanism.

2. Materials and Methods

2.1. Synthesis of MgAl₂O₄ and TiO₂ Nanoparticles

To prepare the MgAl₂O₄ spinel, a modified co-precipitation method followed by the hydrothermal process was used, as shown in Figure 1a. A stoichiometric amount of Mg(NO₃)₂·6H₂O (99.99%, Sigma Aldrich) and Al(NO₃)₃·9H₂O (98%, Honeywell Fluka) was added in deionised water and set to mild stirring conditions until a homogeneous solution formed. An ammonia solution (32%) was used as a precipitating agent, which was added dropwise into the solution with continuous stirring to maintain a pH of at 10.5 because higher PH would have resulted in a lower crystallite size and a higher specific surface area [42]. The stirring and heating continued until the stabilisation of the pH at 10.5 and the appearance of a milky white solution. The solution was then transferred to a hydrothermal autoclave maintained at 160 °C for 24 h and left to cool at room temperature overnight. The precipitates were separated using a centrifuge and washed with warm DI water and absolute ethanol until the pH of the solution reached 7.0 [14]. The slurry was dried at 110 °C overnight. The prepared sample was a ground and calcined in a furnace maintained at 800 °C for 5 h in static air. The collected sample was ground until fine MgAl₂O₄ particles were formed.

In the typical synthesis of TiO₂ nanowires (NWs), 0.70 g of titanium (IV) oxide (99%, Sigma-Aldrich) nano-powder were added in 70 mL of a 10 M solution of NaOH and continuously stirred until the formation of a homogeneous solution. The solution was then shifted to a hydrothermal autoclave, heated to 160 °C for 5 h, and allowed to cool at room temperature. The solution was centrifuged to collect the white precipitates, and then it was washed with a 0.1 M HCl solution and warm deionised water several times to bring the pH to 7.0 [43]. The sample was oven-dried at 110 °C overnight. The collected sample was ground until fine MgAl₂O₄ particles were formed.

2.2. Preparation of Co/TiO₂–MgAl₂O₄ Nanocomposite

A schematic representation of Co/TiO₂–MgAl₂O₄ nanocomposite preparation is shown in Figure 1a. For the preparation of the Co/TiO₂–MgAl₂O₄ nanocomposite, the wetness impregnation method was used with the addition of Co(NO₃)₂·6H₂O (98%, Merck) on MgAl₂O₄ and TiO₂ NW supports. In catalyst preparation, 1.0 g of MgAl₂O₄ and 0.1 g of TiO₂ NWs were dispersed in a 0.1 M Co(NO₃)₂·6H₂O solution and allowed to stir for 5 h at 110 °C. The resulting slurry was oven-dried at 110 °C overnight and calcined at 750 °C for
5 h. The prepared sample was named 5%Co/TiO_{2}–MgAl_{2}O_{4}. Similarly, composite samples of 2.5 and 7.5% Co loading were prepared.

Figure 1. Schematic representation of catalyst preparation (a) synthesis of MgAl_{2}O_{4} (b) synthesis of Co/TiO_{2}–MgAl_{2}O_{4}

2.3. Materials Characterisation

The crystalline structure and phase transition of the prepared catalysts were analysed by the X-ray diffraction method. The identification of the peaks of the calcined and ground samples was carried out via a Bruker D8 advanced X-ray diffractometer with an irradiation wavelength of 1.5418 Å at 40 kV and 40 mA operating conditions. XRD patterns were obtained using diffraction angles over the range of 5–90° with a step size of 0.05°. The Scherrer equation was used to estimate the average crystallite size [44].

The surface morphology of the prepared fresh samples and the spent samples were examined by SEM. To obtain the micro-level images of the samples, a JSM-6490A JEOL SEM (Japan) was used. The resolution of the microscope was set to 3 nm, and it was operated at 30 kV. EDX was used to analyse the elemental composition of catalyst.

TGA was performed using a TGA 5500 from TA Instruments (USA) to observe the thermal stability of the fresh catalyst and the amount of carbon deposited on spent samples by maintaining a nitrogen flow of 25 mL min^{-1} and a heating rate of 10 °C min^{-1} to a maximum temperature at 900 °C. The weight of the sample used for the analysis was 10 mg. The percentage of weight loss was observed at different temperatures based on the reactive carbon.

FTIR was used to identify the functional groups in the sample and the interactions between them. The FTIR analysis was carried out on a Cary 630 FTIR (Agilent Technologies, USA), with the wavenumber ranging from 4000 to 650 cm^{-1}.

2.4. Experimental Setup

The experimental setup scheme for the DRM is illustrated in Figure 2. The fixed bed reactor of PARR (Model # LSP-2.38-0-32-1C-2335EEE, Moline USA) was used for the DRM process. The reactor consisted of a 2.5 ft SS-316 material tube with a \( \frac{1}{2} \) inch diameter. Th tube openings were fixed with SS RED union at both ends and connected to a gas mixer.
The supply of the feed gas was controlled with digital MF4600 series mass flow controllers. The reactor temperature was controlled by the 4871 Series Process Controllers. The K-type thermocouple was used to control the temperature of the catalyst bed. The catalyst was sandwiched in between the glass wool and kept in the centre of the reactor using suitable support. Before each experiment, 60 mL min\(^{-1}\) of N\(_2\) were introduced to purge the reactor system, and 20 mL min\(^{-1}\) of H\(_2\) in the presence of 60 mL min\(^{-1}\) of N\(_2\) gas were used to reduce the catalyst at 750 °C for 1 h by activating the active sites due to the requirement of higher conversions and longer stability runs for the DRM. During experimental runs, the mass flow rates of the feed gas CH\(_4\) (99.99%) and CO\(_2\) (99.99%) were controlled at 10 mL min\(^{-1}\) each and then introduced into the reactor that was set at 750 °C and 0.5 g of catalyst loading. The reaction products were allowed to pass through the condenser before gas analysis. The gases were analysed with a gas chromatograph (GC 2010 plus Shimadzu) equipped with a thermal conductivity detector (TCD) [45]. The temperature of the GC column was set at 200 °C, while the peak retention time was set for 10 min.

\[ \text{CH}_4 \text{conversion} (X_{\text{CH}_4}) = \left( \frac{n_{\text{CH}_4}^{\text{converted}}}{n_{\text{CH}_4}^{\text{feed}}} \times 100 \right) \] (4)

\[ \text{CO}_2 \text{conversion} (X_{\text{CO}_2}) = \left( \frac{n_{\text{CO}_2}^{\text{converted}}}{n_{\text{CO}_2}^{\text{feed}}} \times 100 \right) \] (5)

\[ \text{H}_2 \text{selectivity} (S_{\text{H}_2}) = \left( \frac{n_{\text{H}_2}^{\text{produced}}}{(2 \times n_{\text{CH}_4})^{\text{converted}}} \times 100 \right) \] (6)

\[ \text{CO selectivity} (S_{\text{CO}}) = \left( \frac{n_{\text{CO}}^{\text{produced}}}{(n_{\text{CH}_4} + n_{\text{CO}_2})^{\text{converted}}} \times 100 \right) \] (7)

Figure 2. Schematic representation of the DRM experimental setup.

2.5. Catalytic Activity Calculations

Catalytic activity tests were conducted to analyse the performance and stability of the DRM catalyst in the fixed bed reactor. The DRM activity test included reactant conversion, selectivity, and yield, as presented in Equations (4)–(10). The term ‘n’ represents the number of moles in the following equations.
\[ H_2 \text{ yield} (Y_{H_2})\% = \left( \frac{n_{H_2}^{\text{produced}}}{2 \times (n_{\text{CH}_4}^{\text{feed}})} \right) \times 100 \] (8)

\[ \text{CO yield} (Y_{CO})\% = \left( \frac{n_{CO}^{\text{produced}}}{(n_{\text{CH}_4} + n_{\text{CO}_2})^{\text{feed}}} \right) \times 100 \] (9)

\[ H_2/CO \text{ ratio} = \left( \frac{n_{H_2}^{\text{produced}}}{n_{\text{CO}}^{\text{produced}}} \right) \] (10)

3. Results and Discussion

3.1. Characterization of Catalyst

The XRD of the prepared samples is shown in Figure 3. MgAl\textsubscript{2}O\textsubscript{4} (PDF:21-1152) showed diffraction peaks centred at 2\theta = 31.27°, 36.85°, 44.8, and 65.2° corresponding to different planes with intensified characteristic peaks at 36.85° (hkl;311) with a d-spacing of 0.243 nm and at 65.2° (hkl; 440) with a d-spacing of 0.14 nm, thus indicating the presence of a spinel phase of MgAl\textsubscript{2}O\textsubscript{4} \[46,47\]. A rutile phase with a tetragonal symmetry was detected for TiO\textsubscript{2} (PDF:21-1276) diffraction peaks, with the major phase (211) observed at 54.32° and a d-spacing of 0.16 nm \[48\]. Upon adding cobalt with MgAl\textsubscript{2}O\textsubscript{4}, some peaks observed in MgAl\textsubscript{2}O\textsubscript{4} XRD went missing due to the merging of peaks with the neighbour peaks. Similarly, cubic phase CoAl\textsubscript{2}O\textsubscript{4} (PDF:44-0160) showed a major peak at 36.7° (hkl; 311) with a d-spacing 0.244 nm and a space group of 227:Fd3m, while the other peaks observed at 31.74° and 44.63° with the corresponding planes of (220) and (400), respectively \[49\]. Diffraction peaks were observed at 31.2° and 36.8° with planes (220) and (311), respectively, with a space group of 227:Fd3m of the cubic phase, thus indicating the presence of Co\textsubscript{3}O\textsubscript{4} (PDF:43-1003) \[50\]. CoTiO\textsubscript{3} (PDF:15-0866), with a hexagonal phase with a major peak observed at 32.8° (hkl; 104) and a d-spacing of 0.27 nm, showed the space group of R-3(148) \[51\].

Figure 3. XRD analysis of prepared MgAl\textsubscript{2}O\textsubscript{4}, Co/MgAl\textsubscript{2}O\textsubscript{4}, TiO\textsubscript{2}, and Co/TiO\textsubscript{2}–MgAl\textsubscript{2}O\textsubscript{4} samples.

An SEM micrograph of MgAl\textsubscript{2}O\textsubscript{4} particles is shown in Figure 4a,b, which indicates the formation of porous-structure, block-shaped crystallites depicting the sintering of
particles because of the higher temperature calcination. Figure 4c,d demonstrates the formation of mixed, very fine TiO$_2$ particles and TiO$_2$ nanowires due to the hydrothermal method [52]. Figure 4e,f indicates the modification of MgAl$_2$O$_4$ particles, while Co and TiO$_2$ dispersed over the surface and extended to the pores, ultimately showing a mixed composite structure. The EDXs for MgAl$_2$O$_4$, TiO$_2$, and Co/TiO$_2$–MgAl$_2$O$_4$ are presented in Figure 5a–c. The possible compounds are present in the spectrum, and the extra peaks are associated with carbon tape and gold, that were added during coating before the EDX analysis. The Co loading was confirmed by EDX, as it was presented in the composite.

Figure 4. SEM images of prepared fresh samples: (a,b) 5 and 1 µm of MgAl$_2$O$_4$, (c,d) 5 and 1 µm of TiO$_2$, and (e,f) 5.0 and 1.0 µm of Co/TiO$_2$–MgAl$_2$O$_4$. 
Figure 5. EDS analysis of fresh samples: (a) MgAl2O4, (b) TiO2, and (c) 10 Co/TiO2–MgAl2O4.

Figure 6 shows the thermal stability of the prepared samples. A total of 5% weight loss was observed in the MgAl2O4 sample TGA analysis, as shown in Figure 6a. A weight
loss of 3.5% was observed up to 250 °C because the material was subjected to the removal of the adsorbed moisture and the combustion of nitrates that went unreacted during the reaction, while the rest of the weight loss was due to the dihydroxylation of the mixed oxide to oxides [14]. Furthermore, the TGA analysis of the TiO₂ sample showed a minimal weight loss of up to 2%, thus exhibiting the stability of the sample, and the weight loss was due to adsorbed moisture removal and the decomposition of organic compounds (as presented in Figure 6b), while the slight weight gain after 600 °C was attributed to the rearrangement of the particles after impurity removal and reaction completion. The TGA of the fresh Co/TiO₂–MgAl₂O₄ nanocomposite showed a gradual weight loss up to 5% with the increase in temperature, most of which was rooted in moisture removal, while the sudden weight loss at a high temperature was due to the decomposition of bonds and the formation of the intermediate complexes of a composite, as presented in Figure 6c [14].

Figure 6. TGA analysis of prepared fresh samples: (a) MgAl₂O₄, (b) TiO₂, and (c) Co/TiO₂–MgAl₂O₄.

The FTIR analysis of the prepared fresh samples is shown in Figure 7. The IR spectrum of calcined MgAl₂O₄ observed at 912 cm⁻¹, which corresponded to the stretching vibration of Mg–O–Al falling into inorganic bands and Al–O bonds, was indicative of the crystal MgAl₂O₄ spinel [53–55]. With Co/TiO₂–MgAl₂O₄, two peaks identified at 900 cm⁻¹ corresponded to the vibration of Mg–O–Al, where the peak identified at 744 cm⁻¹ corresponded to O–Ti–O bond stretching vibrations depicting an anatase morphology [56,57] because the band range of 500–800 cm⁻¹ followed the anatase crystal vibration modes [58]. The presence of a small peak around 850 cm⁻¹ corresponded to O–Co–O, which indicated the formation of Co₃O₄ [59]. In the IR spectrum of TiO₂, the small peak was slightly shifted below 700 cm⁻¹, which could have been related to the stretching vibration of Ti–O bonding,
3.2. Dry Reforming of Methane (DRM)

The prepared fresh catalyst samples were loaded into a fixed bed reactor to conduct activity and stability tests during the DRM process. The feed gas ratio was set to 1, with a flow rate of 20 mL min$^{-1}$, and it was fed to reactor maintained at 750 °C with a catalyst loading of 0.5 g.

3.2.1. Catalyst Activity Test

DRM activity test results for the MgAl$_2$O$_4$ and composites with different Co loading are shown in Figure 8a–c. For MgAl$_2$O$_4$, the conversions of CH$_4$ and CO$_2$ were recorded at 61% and 68.5%, respectively. The selectivities of H$_2$ and CO were observed at 17.5% and 26.5%, respectively, whereas the yields of H$_2$ and CO were calculated at 11% and 17%, respectively. The CH$_4$ conversion was observed to be less than the CO$_2$ conversion, while the higher CO$_2$ conversion could be attributed to the basic nature of the support that caused the activation of CO$_2$ [60]. For the Co/TiO$_2$–MgAl$_2$O$_4$, the increase in the conversion of CH$_4$ and CO$_2$ with Co loading could be associated with Co loading that showed a good interaction that formed CoTiO$_3$ and CoAl$_2$O$_4$ with supports, as depicted by the XRD analysis. The higher activity results were due to the higher amount of reduced surface Co sites with increases in cobalt loading [61]. The higher activity results coming with increases in Co loading corresponded with the reduction of Co$_3$O$_4$ at lower temperatures, and XRD analysis confirmed the presence of Co$_3$O$_4$ species. The conversions of CH$_4$ and CO$_2$ were recorded at 68% and 73%, respectively for the composite of 2.5% depicted in Figure 8a. In contrast, 5% of Co loading resulted in conversions of 73% and 78% for CH$_4$ and CO$_2$, respectively, while 7.5% of Co loading resulted in 76% and 83% yields of CH$_4$ and CO$_2$, respectively. A similar trend of increase was shown for H$_2$ and CO selectivity at 2.5–7.5% of Co loading. The highest H$_2$ and CO selectivities recorded for 7.5% of Co loading were 43% and 46.5%, respectively, as presented in Figure 8b. The yields of H$_2$ and CO remained 18% and 22%, respectively, for 2.5% of Co loading, and they were highest at 33% and 37%, respectively, for the 7.5% Co-loaded composite, as demonstrated in Figure 8b.

![Figure 7. FTIR analysis of the prepared fresh samples.](image-url)
Figure 8. Co-loading effect over TiO$_2$/MgAl$_2$O$_4$: (a) conversion ($X_{\text{CH}_4}$ and $X_{\text{CO}_2}$), (b) selectivity ($S_{\text{H}_2}$ and $S_{\text{CO}}$), and (c) yield ($Y_{\text{H}_2}$ and $Y_{\text{CO}}$). Catalyst loading = 0.5 g; reaction temperature = 750 °C; feed ratio (CO$_2$/CH$_4$) = 1; feed flow rate = 20 mL min$^{-1}$.

For the low Co-loaded composite, relatively lower conversions of CH$_4$ and CO$_2$ were observed, primarily due to the presence of CoAl$_2$O$_4$ species, as observed in the XRD analysis, and these were reducible at higher temperatures. However, higher Co-loaded composites had comparatively more easily reducible species, thus resulting in higher activity [62]. Though the higher Co loading adhered with the issue of carbon deposition because the larger amount of available carbon species led to deactivation, in this case, the highest conversions of the 7.5% Co-loaded composite was because of the balance provided by the higher CO$_2$ conversion that provided more oxygen species to the excess carbon formed by the CH$_4$ decomposition [27]. The higher conversion rates of CO$_2$ to CO and oxygen species due to fast reactions resulted in the reaction of the available oxygen species and the high amount of carbon produced with the CH$_4$ decomposition for the highly loaded Co. The result was more CO produced in comparison to H$_2$, as shown by the produced syngas ratio. The 7.5% Co-loaded composite, however, showed a gradual decrease in activity when tested for more extended-run stability tests. However, possible issues connected with high Co-loaded composites include the formation of cobalt clusters that affect support surface properties, and unfavourable gas adsorption conditions with the long-term stability analysis of the 7.5% Co-loaded composite led to the deactivation of the catalyst and, consequently, a lower catalytic activity with time [63]. Thus, considering the better activity and stability results, further tests for conversion, selectivity, yield, and a syngas ratio of over 75 h longer-run stability tests were only conducted for the 5% Co-loaded composite.
To better understand the role of the supports and active metal, as well as their effects on a fully developed catalyst, different catalysts like MgAl\(_2\)O\(_4\), TiO\(_2\), Co/MgAl\(_2\)O\(_4\), Co/TiO\(_2\), and Co/TiO\(_2\)–MgAl\(_2\)O\(_4\) were tested for 5 h TOS for CH\(_4\) and CO\(_2\) conversions, as shown in Figure 9a,b, respectively. Additionally, the H\(_2\) and CO selectivity and the H\(_2\) and CO yield for the prepared catalysts are presented in Figure 10a,b and Figure 11a,b, respectively. The results indicated that TiO\(_2\) resulted in the lowest CH\(_4\) and CO\(_2\) conversion, and the lowest selectivity and yield of H\(_2\) and CO compared to other catalysts because TiO\(_2\), in its pure form in the absence of metal, does not have a significant effect on conversion at higher temperatures but provides good metal–support interactions, as indicated by the formation of a CoTiO\(_3\) intermediate while loading the Co and the provision of good stability [64]. For MgAl\(_2\)O\(_4\) support, CH\(_4\) conversion averaged 61%, while CO\(_2\) conversion averaged approximately 70% over-range during the 5 h TOS, which indicated that inherent basic nature of the MgAl\(_2\)O\(_4\) spinel provided good support and the combined use of Mg and Al could achieve good thermal stability [65]. The basic support aided the dissociation of CO\(_2\) [66]. The results indicated that the use of an MgAl\(_2\)O\(_4\) support could provide decent catalytic results. The lower conversion, selectivity, and yield corresponding to Co/TiO\(_2\) were due to the metallic Co oxidation because the oxidation species (CO\(_2\)) caused catalyst deactivation [67,68]. Co/MgAl\(_2\)O\(_4\) showed intermediate conversions of CH\(_4\) and CO\(_2\), with average values of 65% and 72%, respectively, which could mainly be associated with the formation of CoAl\(_2\)O\(_4\), as discussed in the XRD analysis of Co/MgAl\(_2\)O\(_4\), and was the reason for the inhibition of carbon deposition [69]. The 5% Co/TiO\(_2\)–MgAl\(_2\)O\(_4\) composite showed the maximum conversions of CH\(_4\) and CO\(_2\), along with maximum H\(_2\) and CO selectivity and yield. It is associated to good metal–support interactions that contributed to activity and provided good stability [39]. Due to its basic nature, the presence of the MgAl\(_2\)O\(_4\) support in the composite resulted in CO\(_2\) adsorption and dissociation that produced CO, while the cobalt in the composite aided CH\(_4\) activation to produce more H\(_2\) and surface carbon. The TiO\(_2\) support played role in the reaction of CoTiO\(_3\) species with surface carbon to avoid coke deposition.

![Figure 9](image-url). Effect of time on stream: (a) CH\(_4\) conversion and (b) CO\(_2\) conversion over different prepared fresh samples. Catalyst loading = 0.5 g; reaction temperature = 750 °C; feed ratio (CO\(_2\)/CH\(_4\)) = 1; feed flow rate = 20 mL min\(^{-1}\).
3.2.2. Stability Analysis of Composite

The 5%Co/TiO$_2$–MgAl$_2$O$_4$ was tested for stability analysis over the reaction time of 75 h under the same test conditions. Figure 12a demonstrates that the stability test showed a gradual increase in CO$_2$ and CH$_4$ conversion. The gradual rise was possibly due to the activation of some deposited carbon species. The selectivity of H$_2$ and CO, as presented in Figure 12b, showed the same trend with a gradual rise and then stabilisation for the next phase. The stability in activity was noticed for 75 h on TOS.
The yield of H2 and CO, as presented in Figure 13, showed similar trends to that of selectivity for the 75 h TOS. The H2/CO ratio (Figure 13) value below unity and close to 0.9 was estimated for the 75 h TOS stability test. The H2/CO ratio below unity showed a lower amount of carbon formation and good stability, as a relatively greater amount of CO was produced. The reasons for greater CO production were the faster reaction of carbon with CO2 than CH4 dissociation and the reaction of intermediate CoTiO3 with carbon. Additionally, the possible reaction of H2O produced due to the RWGS reaction (though was not physically observed) with C produced more H2 and CO [70].
3.3. Characterisation of Spent Catalyst

The spent catalyst collected after 75 h of TOS was further analysed and characterised by XRD, TGA, SEM, and EDX. The results are shown in Figures 14 and 15 to investigate the carbon formation over the catalyst. Figure 14a shows that the XRD pattern of the spent catalyst confirmed the presence of the same crystalline phases as those observed in the fresh composite sample, having the same peaks of the MgAl$_2$O$_4$ spinel (PDF#21-1152) with a main peak at 36.85° (hkl; 311). TiO$_2$ (PDF#21-1276) was also observed as the same rutile phase with tetragonal geometry, and its main peak was slightly shifted at 51.8° (hkl; 211). A slight shift in the main peak of CoAl$_2$O$_4$ (PDF#44-0160) was observed at 36.0° (hkl; 311), while Co$_3$O$_4$ (PDF#43-1003) was identified in the fresh sample with peaks at 31.2° (hkl; 220) and 36.8° (hkl; 311). CoTiO$_3$ (PDF#15-0866) indicated a peak at 32.8° (hkl; 104), as observed in the fresh sample. The graphite carbon (PDF#41-1487) with a hexagonal geometry confirmed the peak at 26.3° (hkl; 002) with a d-spacing of 0.337 nm [71]. The TGA profile of the spent catalyst, as shown in Figure 14b, was analysed over three different temperature regions. Column I showed a total 4–5% weight loss up to 300 °C, which could be attributed to the moisture removal and other volatile species [72], where a significant weight loss of almost 14% was observed in column II in a temperature range of 300–500 °C due to the presence of reactive carbon species such as $\alpha$-C and $\beta$-C [73]. Similarly, column III showed a 2–3% weight loss above 500 °C, which could be ascribed to a lower amount of filamentous carbon ($\gamma$-C) formation [3].

Figure 14. Spent catalyst characterization: (a) XRD micrograph, (b) TGA analysis, and (c,d) SEM analysis at 5 and 1 µm, respectively.
3.4. Reaction Mechanism

The overall possible reaction mechanism based on the product and spent catalyst analysis is presented in Figure 16. CH$_4$ activation starts with the adsorption on the active Co surface to produce surface carbon and hydrogen species that then combine to produce hydrogen molecules in the gaseous phase, as represented by reactions (11) and (12) [74,75]. Furthermore, the adsorption of CO$_2$ onto the supports of TiO$_2$ and MgAl$_2$O$_4$ leads to the formation of CoTiO$_3$ species, along with the dissociation of CO$_2$ to CO, as represented by reactions ((13)–(17)). However, the reaction of surface carbon with the CoTiO$_3$ species may result in the formation of CO, as represented by reaction (18).

\[
\text{CH}_4 + 2\text{Co} \rightarrow \text{C} - \text{Co} + \text{H} - \text{Co} \quad (11)
\]
\[
2\text{H} - \text{Co} \rightarrow \text{H}_2 + 2\text{Co} \quad (12)
\]
\[
\text{CO}_2 + \text{MgAl}_2\text{O}_4 \rightarrow \text{O} - \text{MgAl}_2\text{O}_4 + \text{CO} \quad (13)
\]
\[
\text{C} - \text{Co} + \text{O} - \text{MgAl}_2\text{O}_4 \rightarrow \text{MgAl}_2\text{O}_4 + \text{CO} - \text{Co} \quad (14)
\]
\[
\text{CO} - \text{Co} \rightarrow \text{CO} + \text{Co} \quad (15)
\]
\[
\text{CO}_2 + \text{TiO}_2 \rightarrow \text{CO} + \text{TiO}_2 - \text{O} \quad (16)
\]
\[
\text{C} - \text{Co} + \text{O} - \text{TiO}_2 \rightarrow \text{CoTiO}_3 + \text{C} \quad (17)
\]
\[
\text{CoTiO}_3 + \text{C} \rightarrow \text{Co} + \text{TiO}_2 + \text{CO} \quad (18)
\]
Figure 16. Proposed reaction mechanism of the DRM over Co/TiO2–MgAl2O4.

4. Conclusions

This study investigated the synthesis of various Co-loaded, TiO2–MgAl2O4-supported catalysts for the DRM process in a thermally fixed bed reactor. The 5%Co/TiO2–MgAl2O4 showed the best catalytic performance due to its higher CH4 and CO2 conversions, improved selectivity, yield of H2 and CO, and higher stability for more than 75 h TOS. The basic nature of MgAl2O4 helped the activation and dissociation of CO2 and the strong metal–support interaction while adding TiO2 as a co-support. This was evidenced by the formation of CoTiO3 and CoAl2O4 on the catalyst, which improved the conversion of CH4 and, consequently, the catalytic performance. Regardless of the highest CH4 and CO2 conversions of the 5%Co/TiO2–MgAl2O4 among the prepared composites, the H2/CO ratio was below the theoretical ratio. The reaction of CoTiO3 with the reactive carbon to form TiO2 and larger amounts of CO brought the H2/CO ratio to less than unity and improved stability for 75 h TOS. The enhanced stability suggested that this catalyst has prospects for the up-gradation of industrial-scale syngas production when using the DRM process.

Author Contributions: Conceptualization, A.M. and A.H.K.; methodology, A.H.K.; software, S.R.N. and R.L.; validation, S.S., M.H., and M.A.; formal analysis, F.M.; investigation, A.H.K. and M.A.; resources, A.H.K.; data curation, A.K.A.; writing—original draft preparation, A.M. and A.H.K.; writing—review and editing, A.K.A. and S.R.N.; visualization, A.M., R.L.; supervision, A.H.K. and S.R.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the Lab Technologist Qamar-Ud-Din for assistance in the laboratory setup and the facility provided by USPCAS-E, National University of Science and Technology, Pakistan.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Li, X.; Anderson, P.; Jhong, H.-R.M.; Paster, M.; Stubbins, J.F.; Kenis, P.J. Greenhouse gas emissions, energy efficiency, and cost of synthetic fuel production using electrochemical CO2 conversion and the Fischer–Tropsch process. Energy Fuels 2016, 30, 5980–5989. [CrossRef]
2. Nawar, A.; Ali, M.; Khoja, A.H.; Waqas, A.; Anwar, M.; Mahmood, M. Enhanced CO2 capture using organic acid structure modified waste eggshell derived CaO sorbent. J. Environ. Chem. Eng. 2021, 9, 104871. [CrossRef]
3. Khoja, A.H.; Anwar, M.; Shakir, S.; Mehran, M.T.; Mazhar, A.; Javed, A.; Amin, N.A.S. Thermal dry reforming of methane over La2O3 co-supported Ni/MgAl2O4 catalyst for hydrogen-rich syngas production. Res. Chem. Intermed. 2020, 46, 3817–3833. [CrossRef]
4. Khoja, A.H.; Tahir, M.; Amin, N.A.S. Recent developments in non-thermal catalytic DBD plasma reactor for dry reforming of methane. Energy Convers. Manag. 2019, 183, 529–560. [CrossRef]
5. Zaffar, A.; Khan, B.A.; Khoja, A.H.; Khan, U.M.; Sarman, Q.; Mehran, M.T.; Naqvi, S.R.; Ali, M. Synthesis of Ash Derived Co/Zeolite Catalyst for Hydrogen Rich Syngas Production via Partial Oxidation of Methane. Bull. Chem. React. Eng. Catal. 2021. [CrossRef]
6. Dan, M.; Mihet, M.; Lazar, M.D. Hydrogen and/or syngas production by combined steam and dry reforming of methane on nickel catalysts. *Int. J. Hydrogen Energy* **2020**, *45*, 26254–26264. [CrossRef]

7. Khoja, A.H.; Tahir, M.; Amin, N.A.S. Dry reforming of methane using different dielectric materials and DBD plasma reactor configurations. *Energy Convers. Manag.* **2017**, *144*, 262–274. [CrossRef]

8. Khoja, A.H.; Azad, A.K.; Saleem, F.; Khan, B.A.; Naqvi, S.R.; Mehran, M.T.; Amin, N.A. Hydrogen Production from Methane Cracking in Dielectric Barrier Discharge Catalytic Plasma Reactor Using a Nanocatalyst. *Energies* **2020**, *13*, 5921. [CrossRef]

9. Abdulrasheed, A.; Jalil, A.A.; Gambo, Y.; Ibrahim, M.; Hambali, H.; Hamid, M.Y.S. A review on catalyst development for dry reforming of methane to syngas: Recent advances. *Renew. Sustain. Energy Rev.* **2019**, *108*, 175–193. [CrossRef]

10. Aziz, M.; Setiabudi, H.; Teh, I.; ANNuar, N.; Jalil, A. A review of heterogeneous catalysts for syngas production via dry reforming. *J. Taibah Univ. Inst. Chem. Eng.* **2019**, *10*, 139–158. [CrossRef]

11. Selvarajah, K.; Phuc, N.H.H.; Abdullah, B.; Alenazey, F.; Vo, D.-V.N. Syngas production from methane dry reforming over Ni/Al₂O₃ catalyst. *Res. Chem. Interm.* **2016**, *42*, 269–288. [CrossRef]

12. Khoja, A.H.; Tahir, M.; Amin, N.A.S. orming of methane over Ni/Al₂O₃ catalyst. *ChemCatChem* **2016**, *8*, 166–179. [CrossRef]

13. Abdullah, B.; Ghani, N.A.A.; Vo, D.-V.N. Recent advances in dry reforming of methane over Ni-based catalysts. *J. Clean. Prod.* **2017**, *162*, 170–185. [CrossRef]

14. Khoja, A.H.; Tahir, M.; Saidina Amin, N.A. Evaluating the Performance of a Ni Catalyst Supported on La₂O₃-MgAl₂O₄ for Dry Reforming of Methane in a Packed Bed Dielectric Barrier Discharge Plasma Reactor. *Energy Fuels* **2019**, *33*, 11630–11647. [CrossRef]

15. Usman, M.; Daud, W.M.A.W. Microemulsion based synthesis of Ni/MgO catalyst for dry reforming of methane. *RSC Adv.* **2016**, *6*, 38277–38289. [CrossRef]

16. Wu, J.J.; Zhou, X.D. Catalytic conversion of CO₂ to value added fuels: Current status, challenges, and future directions. *Chin. J. Catal.* **2016**, *37*, 999–1015. [CrossRef]

17. Löffberg, A.; Guerrero-Caballero, J.; Kane, T.; Rubbens, A.; Jalowiecki-Duhamel, L. Ni/CoO₂ based catalysts as oxygen vectors for the chemical looping dry reforming of methane for syngas production. *Appl. Catal. B Environ.* **2017**, *212*, 159–174. [CrossRef]

18. Aramouni, N.A.K.; Touma, J.G.; Tarboush, B.A.; Naqvi, S.R.; Mehran, M.T.; Amin, N.A. Hydrogen Production from Methane Cracking in Dielectric Barrier Discharge Catalytic Plasma Reactor Using a Nanocatalyst. *Energies* **2020**, *13*, 5921. [CrossRef]

19. Yentekakis, I.V.; Goula, G.; Hatzisymeon, M.; Betsi-Argyropoulou, I.; Botzolaki, G.; Kousi, K.; Kondarides, D.I.; Taylor, M.J.; Parlett, C.M.; Osatiashtiani, A. Effect of support oxygen storage capacity on the catalytic performance of Rh nanoparticles for CO₂ reforming of methane. *Appl. Catal. B Environ.* **2019**, *243*, 490–501. [CrossRef]

20. Wittich, K.; Krämer, M.; Bottke, N.; Schunk, S.A. Catalytic Dry Reforming of Methane: Insights from Model Systems. *ChemCatChem* **2020**, *12*, 1818–1837. [CrossRef]

21. García-Diéguez, M.; Pieta, I.; Herrera, M.; Larrubia, M.; Alemany, L. Nanostructured Pt-and Ni-based catalysts for CO₂-reforming of methane. *J. Catal.* **2020**, *400*, 136–145. [CrossRef]

22. Izquierdo, U.; Barrio, V.; Bizkarra, K.; Gutierrez, A.; Arraib, J.; Gartzia, I.; Bañuelos, J.; Lopez-Arbeloa, I.; Cambra, J. Ni and RhNi catalysts supported on Zeolites L for hydrogen and syngas production by biogas reforming processes. *Chem. Eng. J.* **2014**, *238*, 178–188. [CrossRef]

23. Tahir, M.; Tahir, B.; Amin, N.A.S.; Muhammad, A. Photocatalytic CO₂ methanation over NiO/I₂O₃ promoted TiO₂ nanocatalysts using H₂O and/or H₂ reductants. *Mang. Engin.* **2016**, *119*, 368–378. [CrossRef]

24. Zhou, L.; Li, L.; Wei, N.; Li, J.; Basset, J.M. Effect of NiAl₂O₄ formation on Ni/Al₂O₃ stability during dry reforming of methane. *ChemCatChem* **2015**, *7*, 2508–2516. [CrossRef]

25. Das, S.; Thakur, S.; Bag, A.; Gupta, M.S.; Mondal, P.; Bordoloi, A. Support interaction of Ni nanocluster based catalysts applied in CO₂ reforming. *J. Catal.* **2015**, *330*, 46–60. [CrossRef]

26. Christensen, K.O.; Chen, D.; Ledeng, R.; Holmen, A. Effect of supports and Ni crystal size on carbon formation and sintering during steam methane reforming. *Appl. Catal. A Gen.* **2006**, *314*, 9–22. [CrossRef]

27. Budiman, A.W.; Song, S.-H.; Chang, T.-S.; Shin, C.-H.; Choi, M.-J. Dry reforming of methane over cobalt catalysts: A literature review of catalyst development. *Catal. Surf. Asia* **2012**, *16*, 183–197. [CrossRef]

28. Ewbank, J.L.; Kovarik, L.; Kevins, C.C.; Sievers, C. Effect of preparation methods on the performance of Co/Al₂O₃ catalysts for dry reforming of methane. *Green Chem.* **2014**, *16*, 885–896. [CrossRef]

29. Abasaedd, A.E.; Al-Fatehs, A.S.; Naeem, M.A.; Ibrahim, A.A.; Fakeeha, A.H. Catalytic performance of CeO₂ and ZrO₂ supported Co catalysts for hydrogen production by dry reforming of methane. *Int. J. Hydrogen Energy* **2015**, *40*, 6818–6826. [CrossRef]

30. Ferencz, Z.; Bará, K.; Oszkó, A.; Kónya, Z.; Kecskés, T.; Erdőhegyi, A. Dry reforming of CH₄ on Rh doped Co/Al₂O₃ catalysts. *Catal. Today* **2014**, *228*, 123–130. [CrossRef]

31. el Hassan, N.; Kaydouh, M.; Geagea, H.; el Zein, H.; Jabbour, K.; Casale, S.; el Zakhem, H.; Massiani, P. Low temperature dry reforming of methane on rhodium and cobalt based catalysts: Active phase stabilization by confinement in mesoporous SBA-15. *Appl. Catal. A Gen.* **2016**, *520*, 114–121. [CrossRef]

32. Usman, M.; Daud, W.M.A.W.; Abbas, H.F. Dry reforming of methane: Influence of process parameters-A review. *Renew. Sustain. Energy Rev.* **2015**, *45*, 710–744. [CrossRef]
33. Khoja, A.H.; Tahir, M.; Amin, N.A.S. Process optimization of DBD plasma dry reforming of methane over Ni/La2O3MgAl2O4 using multiple response surface methodology. *Int. J. Hydrogen Energy* 2019, **44**, 11774–11787. [CrossRef]

34. di Michele, A.; Dell'Angelo, A.; Tripodi, A.; Bahadori, E.; Sanchez, F.; Motta, D.; Dimitratos, N.; Rossetti, I.; Ramis, G. Steam reforming of ethanol over Ni/MgAl2O4 catalysts. *Int. J. Hydrogen Energy* 2019, **44**, 952–964. [CrossRef]

35. Medeiros, R.L.; Macedo, H.P.; Melo, V.R.; Oliveira, Â.A.; Barros, J.M.; Melo, M.A.; Melo, D.M. Ni supported on Fe-doped MgAl2O4 for dry reforming of methane: Use of factorial design to optimize H2 yield. *Int. J. Hydrogen Energy* 2016, **41**, 14047–14057. [CrossRef]

36. Safari, J.; Akbari, Z.; Naseh, S. Nanocrystalline MgAl2O4 as an efficient catalyst for one-pot synthesis of multisubstituted imidazoles under solvent-free conditions. *J. Saudi Chem. Soc.* 2016, **20**, S250–S255. [CrossRef]

37. Hadian, N.; Rezaei, M.; Mosayebi, Z.; Meshkani, F. CO2 reforming of methane over nickel catalysts supported on nanocrystalline MgAl2O4 with high surface area. *J. Nat. Gas Chem.* 2012, **21**, 200–206. [CrossRef]

38. Seo, H.O.; Sim, J.K.; Kim, K.-D.; Kim, Y.D.; Lim, D.C.; Kim, S.H. Carbon dioxide reforming of methane to synthesis gas over a TiO2–Ni inverse catalyst. *Appl. Catal. A Gen.* 2013, **451**, 43–49. [CrossRef]

39. Abbas, T.; Tahir, M.; Saidina Amin, N.A. Enhanced metal–support interaction in Ni/Co/TiO2 nanorods toward stable and dynamic hydrogen production from phenol steam reforming. *Ind. Eng. Chem. Res.* 2018, **58**, 517–530. [CrossRef]

40. Khoja, A.H.; Tahir, M.; Amin, N.A.S. Process optimization of DBD plasma dry reforming of methane over Ni/La2O3MgAl2O4 spinel coating on graphite surface to improve its water-wettability and oxidation resistance. *Ceram. Int.* 2009, **35**, 457–461. [CrossRef]

41. Shehzad, N.; Tahir, M.; Johari, K.; Murugesan, T.; Hussain, M. A critical review on TiO2 based photocatalytic CO2 reduction system: Strategies to improve efficiency. *J. CO2 Util.* 2018, **26**, 98–122. [CrossRef]

42. Mosayebi, Z.; Rezaei, M.; Hadian, N.; Kordshuli, F.Z.; Meshkani, F. Low temperature synthesis of nanocrystalline magnesium alumina with high surface area by surfactant assisted precipitation method: Effect of preparation conditions. *Mater. Res. Bull.* 2012, **47**, 2154–2160. [CrossRef]

43. Sanjabi, S.; Obeydavi, A. Synthesis and characterization of nanocrystalline MgAl2O4 spinel via modified sol–gel method. *J. Alloys Compd.* 2011, **517**, 517–530. [CrossRef]

44. Wang, Y.; Wang, S.; Yu, X.; Tang, S.; Han, S.; Yang, L. Irradiation synthesis and characterization of CoAl2O4: Ce phosphors. *Optik* 2020, **210**, 165408. [CrossRef]

45. Zhou, Y.; Wang, Y.; Wang, J.; Lin, L.; Wu, X.; He, D. Controlled synthesis and characterization of hybrid Sn-doped Co3O4 nanowires for supercapacitors. *Mater. Lett.* 2018, **216**, 248–251. [CrossRef]

46. Wang, Q.; Guo, Q.; Wang, L.; Li, B. The flux growth of single-crystalline CoTiO3 polyhedral particles and improved visible-light photocatalytic activity of heterostructured CoTiO3/g-C3N4 composites. *Dalton Trans.* 2016, **45**, 17748–17758. [CrossRef]

47. Tahir, M.N.; Andre, R.; Sahoo, J.K.; Jochum, F.D.; Theato, P.; Natalio, F.; Berger, R.; Brandscheid, R.; Kolb, U.; Tremel, W. Hydrogen peroxide sensors for cellular imaging based on horse radish peroxidase reconstituted on polymer-functionalized TiO2 nanorods. *Nanoscale* 2011, **3**, 3907–3914. [CrossRef] [PubMed]

48. Thanabodeekij, N.; Sathupunya, M.; Jamieson, A.M.; Wongkasemjit, S. Correlation of sol–gel processing parameters with microstructure and properties of a ceramic product. *Mater. Charact.* 2003, **50**, 325–337. [CrossRef]

49. Adak, A.; Saha, S.; Pramanik, P. Synthesis and characterization of MgAl 2 O 4 spinel by PVA evaporation technique. *J. Mater. Sci. Lett.* 1997, **16**, 234–235. [CrossRef]

50. Sanjabi, S.; Obeydavi, A. Synthesis and characterization of nanocrystalline MgAl2O4 spinel via modified sol–gel method. *J. Alloys Compd.* 2015, **645**, 535–540. [CrossRef]

51. Tai, J.Y.; Leong, K.H.; Saravanam, P.; Aziz, A.A.; Sim, L.C. Dopant-free oxygen-rich titanium dioxide: LED light-induced photocatalysis and mechanism insight. *J. Mater. Sci.* 2017, **52**, 11630–11642. [CrossRef]

52. Etacheri, V.; Seery, M.K.; Hinder, S.J.; Pillai, S.C. Oxygen rich titania: A dopant free, high temperature stable, and visible-light active anatase photocatalyst. *Adv. Funct. Mater.* 2011, **21**, 3744–3752. [CrossRef]

53. Sim, L.C.; Tan, W.H.; Leong, K.H.; Bashir, M.J.; Saravanam, P.; Surib, N.A. Mechanistic characteristics of surface modified organic semiconductor g-C3N4 nanotubes alloyed with titania. *Materials* 2017, **10**, 28. [CrossRef] [PubMed]
59. Prabaharan, D.D.M.; Sadaiyandi, K.; Mahendran, M.; Sagadevan, S. Precipitation method and characterization of cobalt oxide nanoparticles. *Appl. Phys. A* 2017, 123, 264. [CrossRef]

60. Domínguez, A.; Fernández, Y.; Fidalgo, B.; Pis, J.; Menéndez, J. Biogas to syngas by microwave-assisted dry reforming in the presence of char. *Energy Fuels* 2007, 21, 2066–2071. [CrossRef]

61. Tavasoli, A.; Sadaghiani, K.; Nakhaeipour, A.; Ahangari, M. Cobalt loading effects on the structure and activity for Fischer-Tropsch and water-gas shift reactions of Co/Al2O3 catalysts. *Iran. J. Chem. Chem. Eng.* 2007, 26, 9–16.

62. Wang, W.-J.; Chen, Y.-W. Influence of metal loading on the reducibility and hydrogenation activity of cobalt/alumina catalysts. *Appl. Catal.* 1991, 77, 223–233. [CrossRef]

63. Zhang, G.; Su, A.; Du, Y.; Qu, J.; Xu, Y. Catalytic performance of activated carbon supported cobalt catalyst for CO2 reforming of CH4. *J. Colloid Interface Sci.* 2014, 433, 149–155. [CrossRef] [PubMed]

64. Baamran, K.S.; Tahir, M. Ni-embedded TiO2-ZnTiO3 reducible perovskite composite with synergistic effect of metal/support towards enhanced H2 production via phenol steam reforming. *Energy Convers. Manag.* 2019, 200, 112064. [CrossRef]

65. Zhang, J.; Wang, H.; Dalai, A.K. Effects of metal content on activity and stability of Ni-Co bimetallic catalysts for CO2 reforming of CH4. *Appl. Catal. A Gen.* 2008, 339, 121–129. [CrossRef]

66. Seo, H.O. Recent scientific progress on developing supported Ni catalysts for dry (CO2) reforming of methane. *Catalysts* 2018, 8, 110. [CrossRef]

67. Takanabe, K.; Nagaoka, K.; Nariai, K.; Aika, K. Influence of reduction temperature on the catalytic behavior of Co/TiO2 catalysts for CH4/CO2 reforming and its relation with titania bulk crystal structure. *J. Catal.* 2005, 230, 75–85. [CrossRef]

68. Nagaoka, K.; Takanabe, K.; Aika, K. Modification of Co/TiO2 for dry reforming of methane at 2 MPa by Pt, Ru or Ni. *Appl. Catal. A Gen.* 2004, 268, 151–158. [CrossRef]

69. Xu, L.; Zhang, J.; Wang, F.; Yuan, K.; Wang, L.; Wu, K.; Xu, G.; Chen, W. One-step synthesis of ordered mesoporous CoAl2O4 spinel-based metal oxides for CO2 reforming of CH4. *RSC Adv.* 2015, 5, 48256–48268. [CrossRef]

70. Salvador, F.; Sánchez-Montero, M.J.; Izquierdo, C. C/H2O reaction under supercritical conditions and their repercussions in the preparation of activated carbon. *J. Phys. Chem. C* 2007, 111, 14011–14020. [CrossRef]

71. Guler, M.; Dogu, T.; Varisili, D. Hydrogen production over molybdenum loaded mesoporous carbon catalysts in microwave heated reactor system. *Appl. Catal. B Environ.* 2017, 219, 173–182. [CrossRef]

72. Chong, C.C.; Setiabudi, H.D.; Jalil, A.A. Dendritic fibrous SBA-15 supported nickel (Ni/DFSBA-15): A sustainable catalyst for hydrogen production. *Int. J. Hydrogen Energy* 2020, 45, 18533–18548. [CrossRef]

73. Al-Fatesh, A.S.; Naeem, M.A.; Fakeeha, A.H.; Abasaeed, A.E. Role of La2O3 as promoter and support in Ni/γ-Al2O3 catalysts for dry reforming of methane. *Chin. J. Chem. Eng.* 2014, 22, 28–37. [CrossRef]

74. Fan, M.S.; Abdullah, A.Z.; Bhatia, S. Catalytic technology for carbon dioxide reforming of methane to synthesis gas. *ChemCatChem* 2009, 1, 192–208. [CrossRef]

75. Topalidis, A.; Petrakis, D.; Ladavos, A.; Loukatzikou, L.; Pomonis, P. A kinetic study of methane and carbon dioxide interconversion over 0.5% Pt/SrTiO3 catalysts. *Catal. Today* 2007, 127, 238–245. [CrossRef]