Catalytic Decomposition of 2% Methanol in Methane over Metallic Catalyst by Fixed-Bed Catalytic Reactor

Ali Awad 1,2,* , Israr Ahmed 3 , Danial Qadir 2 , Muhammad Saad Khan 4 and Alamin Idris 5 ,* 

1 Department of Chemical Engineering, University of Faisalabad, Faisalabad 38000, Pakistan
2 Chemical Engineering Department, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Malaysia; daniel_g02660@utp.edu.my
3 School of Chemical and Material Engineering, National University of Science and Technology, Islamabad 44000, Pakistan; israr.ahmed@scme.nust.edu.pk
4 Mechanical Engineering Department, Texas A&M University at Qatar, Al Rayyan 5270, Qatar; muhammad_saad.khan@qatar.tamu.edu
5 Department of Engineering and Chemical Sciences, Karlstad University, 651 88 Karlstad, Sweden

* Correspondence: ali.awad@tuf.edu.pk (A.A.); alamin.abdulgadir@kau.se (A.I.); Tel.: +46-54-700-1785 (A.I.)

Abstract: The structure and performance of promoted Ni/Al 2 O 3 with Cu via thermocatalytic decomposition (TCD) of CH 4 mixture (2% CH 3 OH) were studied. Mesoporous Cat-1 and Cat-2 were synthesized by the impregnation method. The corresponding peaks of nickel oxide and copper oxide in the XRD showed the presence of nickel and copper oxides as a mixed alloy in the calcined catalyst. Temperature program reduction (TPR) showed that Cu enhanced the reducibility of the catalyst as the peak of nickel oxide shifted toward a lower temperature due to the interaction strength of the metal particles and support. The impregnation of 10% Cu on Cat-1 drastically improved the catalytic performance and exhibited 68% CH 4 conversion, and endured its activity for 6 h compared with Cat-1, which deactivated after 4 h. The investigation of the spent catalyst showed that various forms of carbon were obtained as a by-product of TCD, including graphene fiber (GF), carbon nanofiber (CNF), and multi-wall carbon nanofibers (MWCNFs) on the active sites of Cat-2 and Cat-1, following various kinds of growth mechanisms. The presence of the D and G bands in the Raman spectroscopy confirmed the mixture of amorphous and crystalline morphology of the deposited carbon.

Keywords: alloys; carbon nanofiber; catalyst; clean energy; premixed gas

1. Introduction

The need for less harmful and more efficient sources of fuel has gained interest in recent years [1]. The continuous combustion of fossil fuels used in industries to satisfy energy demands has contributed to the emission of contaminants and greenhouse gases, such as CO X , NO X , and SO X . Thus, it is imperative to find an alternative renewable source of energy, i.e., hydrogen (H 2 ). H 2 is considered one of the most promising and energy-efficient fuels that can be converted into clean energy effectively [2,3]. Presently, H 2 is used in various engineering applications, such as NH 3 production, oil refineries, and CH 3 OH production plants [4].

Various methods to produce H 2 have been developed, which include dry reforming, partial oxidation, and steam reforming of CH 4 [5–7]. Ammonia decomposition was also proposed as an effective technique for hydrogen production [8]. However, the low purity of H 2 and substantial emissions of CO 2 restrict their practical applications [9]. Thermocatalytic decomposition (TCD) of methane has gained interest among researchers over the last decade, as it is a single-step decomposition process. Still, high operating parameters and poor catalyst stability limit its industrial applications. Catalytic decomposition of CH 4 is an endothermic technique that produces hydrogen without CO X emissions, which simplifies the process significantly and reduces the overall process cost [10]. Furthermore, the value-added carbon in the form of carbon nanofiber (CNF), bi-wall carbon nanofiber (BWCNF),
carbon nanotube (CNT), and multi-wall carbon nanotube (MWCNT) is the only by-product of this process [11,12]. The TCD of CH₄ is a non-oxidative decomposition technique that faces many challenges in the form of high reaction temperature due to the high bond energy of CH₄, which has an enthalpy of 74.52 kJmol⁻¹ [13]. The mechanistic preview of the reaction state is a four-step reaction, where the attachment/diffusion of methane on the surface of the catalyst is the binary step, followed by the breakage of C-H atoms as the main step, as high energy is required to break the sp³-hybridized carbon hydrogen bond. The next step is the conversion of hydrogen atoms to a stabilized molecule, and in the last stage, the carbon attached to the surface of the catalysts is transformed into various forms, such as GF, CNF, and MWCNF, depending on the material composition and reaction parameters.

One of the effective methods to reduce this high reaction temperature is by using transition metals (Ni, Cu, Co, and Fe) as catalysts [14]. However, carbon produced as a by-product encapsulates the active sites of the catalyst, which causes rapid deactivation and opens new horizons for research in this field [15]. The selection of catalysts is crucial in the TCD process for H₂ generation, so the improvements in the composition and properties have a substantial effect on the sustainability of the current process [16]. Various solutions have been presented for the optimization of TCD. This can be achieved by altering the physicochemical properties and composition of the catalysts, and amending the reaction conditions, such as reaction temperature, gas hourly space velocity, and the weight of the catalyst. Moreover, the practice of using admixtures and premixed gases as feedstocks was also suggested as an active solution to enhancing the effectiveness of TCD [17].

The types of catalysts that are used in the catalytic decomposition of methane processes are metallic and carbonaceous materials [18]. However, carbonaceous catalysts exhibit lower CH₄ consumption and reaction rates compared with metallic catalysts; hence, they are not employed frequently [19]. The most common metals used for the catalytic decomposition of CH₄ are the transition metals with partially filled d orbitals. These metals are mixed with porous supports, such as Al₂O₃, MgO, Fe₂O₃, and CeO₂, using various synthesis methods, including impregnation, co-precipitation, and sol-gel [20,21]. Of all the transition metals, Ni is frequently employed in reforming reactions due to its reactive nature, easy availability and because it is relatively less expensive, but its early deactivation limits its applications. Therefore, the modification of Ni-based catalysts with other transition metals is essential for improving the stability of the catalysts. Various metals such as Cu, Pd, Mg, Mo, Fe, Co, and Cr are impregnated on a Ni-based catalyst, thus forming mixed-metal alloys [22]. Thus, they proved to be very effective catalysts in maintaining the equilibrium of the TCD.

The study of the thermocatalytic decomposition of CH₄ with other gases was also proposed as an active method of improving catalyst stability and activity [23]. Hence, the TCD of CH₄ with various hydrocarbons as feedstock has been widely explored [24]. The study of TCD with 2% CH₃OH/CH₄ was explored in our previous publication over Ni/Al₂O₃ [25]. We found that the CH₄ decompositions improved by increasing the metal loadings and reaction temperatures. The existence of 2% CH₃OH improved the activity of the material, and its catalytic stability was significantly enhanced. Similarly, the effect of bimetallic catalysts on TCD was investigated in our previous study [26]. The study showed that the addition of Pd on a Ni-based catalyst improved the catalyst stability and activity significantly when we used 2% CH₃OH/CH₄ premixed feedstock.

In our previous publication, we reported the results of 15% Cu on a Ni-based catalyst for hydrogen production over TCD of methane and methanol mixture [27]. We concluded that the addition of 2% methanol enhanced the catalytic activity of the material. Thus, we decided to test another Cu-based catalyst over premixed feedstock. Hence, in this study, we investigated the use of Cu as an effective promoter on the effectiveness of a Ni-based catalyst by using a novel premixed feedstock 2% CH₃OH/CH₄ over a high temperature fixed-bed catalytic reactor. Furthermore, the physicochemical properties of fresh and spent promoted catalysts were also explored using various microscopy techniques. Although
several metallic catalysts have already been tested for the TCD of methane, this research work focused on the testing of the TCD over premixed gas, where only a handful of research studies have been accomplished.

2. Materials and Methods

2.1. Materials

The materials, which included 2% CH$_3$OH/CH$_4$, H$_2$, and N$_2$ with a purity of 99.99%, were purchased from Malaysia Linde Limited (Ipoh, Malaysia). H$_2$ was used as a pretreatment gas for catalyst activation, and N$_2$ was used as purging gas with the feedstock. Nickel nitrate hexahydrate and copper nitrate trihydrate were used as nickel and copper precursors, whereas γ-Al$_2$O$_3$ was used as the material support. Ni (NO$_3$)$_2$.6H$_2$O was purchased from Bendosen Chemicals (Johor, Malaysia); Cu (NO$_3$)$_2$.3H$_2$O and γ-Al$_2$O$_3$ were purchased from R&M Chemicals (Selangor, Malaysia).

2.2. Catalyst Synthesis

Monometallic catalyst Cat-1 was prepared by the wet impregnation technique and treated as a reference catalyst. The bimetallic catalyst Cat-2, containing 10% Cu supported on γ-Al$_2$O$_3$, was also synthesized by the same technique at an overall 50% concentration of Ni in the catalyst weight, as per calculated amounts of Ni (NO$_3$)$_2$.6H$_2$O, Cu (NO$_3$)$_2$.3H$_2$O used. The metal precursors were dissolved in H$_2$O and, later, the calculated amount of γ-Al$_2$O$_3$ as support was added. The mixture was gently mixed and evaporated at 363 K using a magnetic stirrer at 400 rpm for 3 h, dried at 383 K overnight, and calcined at 873 K for 4 h [27]. The catalyst tagging is explained in Table 1.

2.3. Catalyst Characterization

The analytic properties of the catalyst were studied via BET, X-ray diffraction (XRD), H$_2$ temperature-programmed reduction (H$_2$-TPR), field emission electron microscope (FESEM), transmission electron microscope (TEM), and Raman spectroscopy. The detailed information on the specifications of the analytical equipment employed in this research work can be found in [27,28].

2.4. Catalyst Evaluation

The catalytic decomposition runs over the synthesized catalysts were carried out by using a fixed-bed catalytic reactor, as previously performed in our group [23]. A catalyst weight of 0.1 g was appropriately sieved and sandwiched in the center of the steel pipe of the reactor by employing quartz wool. The catalyst was activated with H$_2$ at 15,000 mL g$_{cat}^{-1}$ h$^{-1}$ and 873 K for 2 h. The catalytic runs were carried out at atmospheric pressure and 1023 K, using a premixed feedstock of 2% CH$_3$OH/CH$_4$ diluted with N$_2$. The composition of gaseous products was analyzed using Agilent 7820A series gas chromatography. The calibrated data were used to calculate the concentrations of H$_2$, N$_2$, CH$_3$OH, and CH$_4$ in the post-reaction gaseous mixture and, finally, the reactor was purged with N$_2$ and cooled to room temperature. The reactor configuration can be found in our previous paper [29].
3. Results

3.1. Characterization of Fresh Catalyst

3.1.1. BET Study

The textural characteristics of Cat-1 and Cat-2, as determined by BET, showed a noticeable variation in the textural properties in the promoted Ni-based catalyst. This observation is rational due to the successful impregnation of NiO and CuO in the porous structure of γ-Al₂O₃. The surface area of the commercially available alumina that we employed in our research group was 7.66 m²g⁻¹. The BET surface area of Cat-1 (5.15 m²g⁻¹) dropped by adding 10% Cu (4.96 m²g⁻¹) due to the partial obstruction of pores on the surface of the support by metal precursors [30]. The pore volume and pore diameter also changed from 0.011 to 0.018 cm³ g⁻¹ and 8.90 to 14.80 nm by adding Cu on the Cat-1. The change in the texture properties of Cat-2 can be related to the agglomeration of particles, very similar findings are also reported in [23], where the surface area decreased after successful impregnation of Cu over Ni-based catalysts.

3.1.2. XRD Study

The XRD diffractograms of Cat-1 and Cat-2 were employed to identify various phases in the calcined catalysts, as shown in Figure 1, over a range of 2θ = 0–90°. For both catalysts, the reflections at 2θ of 25°, 35°, 44°, 55°, 58°, and 66° were associated with the γ-Al₂O₃ phase [10]. The relative intensity of all peaks of γ-Al₂O₃ lessened after the Ni and Cu impregnations. This observation can be linked with the enhancement of the metal dispersion on the γ-Al₂O₃ support. Moreover, the peaks at 2θ of 37.4°, 64.3°, 75.3°, and 79° appeared as a result of the cubic NiO phase for both Ni-based catalysts. In the XRD diffractograms of Cat-2, no independent diffraction peaks of CuO were observed; rather, the relative intensities of NiO increased. The increase in the intensity of the NiO peaks showed that in the promoted catalyst, CuO and NiO possess identical peaks overlapping each other. Thus, they form mixed oxides (Niₓ(O₁₋ₓ)CuₓO) [31]. Similar findings were reported in the literature [32] where the authors explained that, after the successful impregnations of Cu, the relative intensities of NiO increased, thus confirming the formation of mixed oxides.

![Figure 1. X-ray diffraction for a fresh catalyst.](image-url)
3.1.3. H₂-TPR Study

The H₂-TPR study of Cat-1 and Cat-2, as shown in Figure 2, was carried out to investigate the reducibility of active metal oxides. A broader peak at a range of 600–800 K of Cat-1 exhibited the reduction of strongly interacted NiO with γ-Al₂O₃ support. The whole reduction of NiO into metallic Ni° was achieved here. The reduction of NiO is shown in Equation (1) [33].

\[
\text{NiO} + \text{H}_2 \rightarrow \text{Ni}° + \text{H}_2\text{O} \quad (1)
\]

Cat-2 shows three H₂ consumption peaks at 560, 700, and 840 K. The first peak at 500 K corresponds to the interaction of the Cu and Al₂O₃ supports, while the second sharp peak at 650 K ascribes to the reduction of the Ni–Cu alloy. The last peak at 900 K can be associated to the reduction of Ni that had a strong interaction with the support. It can be seen (c.f. Figure 2) that the Cu addition shifted the TPR profile of NiO to a lower temperature as the addition of a promoter on the Cat-1 catalyst improved its degree of reducibility. The same reduction improvement was also reported when a Cu promoter was used in a Cat-1 catalyst [34,35]. The reduction of CuO at 500 K converted a H₂ molecule into atomic hydrogen, which assisted the reduction of NiO at a lower temperature range by a spillover effect, hence the shifting of the H₂-TPR peaks of NiO to lower temperatures. The H₂-TPR of CuO is shown in Equation (2).

\[
\text{CuO} + \text{H}_2 \rightarrow \text{Cu}° + \text{H}_2\text{O} \quad (2)
\]

Figure 2. The temperature-programmed reduction for fresh catalyst.

3.1.4. FESEM Images

The surface morphology of the Ni-based material and the Cu-promoted Cat-2 catalysts, as shown in Figure 3, shows the dissemination of uneven and nonuniform particles on γ-Al₂O₃ supports. The FESEM images show that the particle distribution of both catalysts was in the nanoscale, while more tightly aggregated nanoparticles were seen in Cat-2. Moreover, the particle size of the prepared catalysts ranged from 25–100 nm. The agglomerations and larger particles were observed more often in promoted catalysts due to their high metal loadings, and from the successful addition of Cu on the Cat-1 [36]. Moreover, FESEM analysis confirmed that larger particle size and more aggregated distribution of the nanocatalyst particles would result in lower BET surface area.
3.2. Catalytic Cracking Reforming Evaluation

The TCD of 2% CH$_3$OH/CH$_4$ over Cat-1 and Cat-2 was studied at a temperature of 1023 K and a feedstock flow rate of 18,000 mL g$_{\text{cat}}^{-1}$ h$^{-1}$ using 0.1 g of material, as shown in Figure 4. The TCD of CH$_4$ is an endothermic process, and the performance of the catalyst is enhanced by an increase in reaction temperature [37]. Moreover, Cat-1-type materials are extensively used in hydrocarbon cracking and reforming reactions [38]; however, they are sensitive to reaction temperatures and are subject to rapid deactivation at high temperatures [39]. In the TCD reaction, along with H$_2$ as the desired product, an ample amount of carbon was also deposited on the surface of the catalyst. Hence, the inability of Ni° to diffuse coke leads to the formation of the encapsulating layer of carbon around the active sites, thus deactivating the catalyst [35]. A similar observation was made in a recent work, in which Cat-1 was deactivated after 4 h, resulting in 26% CH$_4$ conversion at 1023 K and GHSV 18,000 mL g$_{\text{cat}}^{-1}$ h$^{-1}$ using 0.1 g of catalyst (c.f. Figure 4).

Various efforts were made to synthesize stable and high carbon resistant bi-metallic promoted Ni-based catalysts. The alloying and synergistic effect between Ni and promoter boosted the CH$_4$ conversions and carbon resistance ability of the catalyst drastically. The addition of metal additive Cu (10%) on the performance of Cat-1 was explored in recent work (c.f. Figures 4 and 5). The formation of mixed oxides during calcination of Ni$_x$Cu$_{(1-x)}$O and Ni-Cu alloy after H$_2$ reduction considerably affects the performance of
the promoted catalyst [40]. It was explained that carbon has a higher affinity with Cu\(^{\circ}\), and
the rate of carbon diffusion in Cu\(^{\circ}\) is relatively higher compared with Ni\(^{\circ}\). Hence, instead of forming an encapsulation layer, it diffuses in the promoter [32]. In Cat-2, Cu acted like a carbon reservoir to maintain the equilibrium between formed and diffused carbon and kept the surface of Ni\(^{\circ}\) fresh for the conversion of CH\(_4\) into H\(_2\) and elemental carbon. Hence, the addition of 10% Cu on Cat-1 increased the CH\(_4\) conversions from 26% to 68%, and the catalyst sustained its stability for 6 h (c.f. Figure 4). It has also been observed that small methanol plays a significant role in maintaining the catalytic stability of the catalyst. Generally, apart from the decomposition of CH\(_3\)OH into the mixture of CO and H\(_2\) and a series of reactions, including a reverse water gas reaction, a methanation reaction also occurred, as shown in Equations (3)–(6) [41,42].

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CO} + 2\text{H}_2 \quad (3) \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (4) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (5) \\
\text{C} + \text{CO}_2 & \rightarrow 2\text{CO} \quad (6)
\end{align*}
\]

The role of CH\(_3\)OH is to maintain the catalytic ability by linking it to the partial regeneration of the catalyst [43]. There are various approaches to catalyst regeneration, in which the carbon encapsulated on the catalyst can be oxidized into CO\(_2\) and CO [44]. The mechanism of CH\(_3\)OH decomposition is complex as various reactions occur concurrently, resulting in an assortment of products. CH\(_3\)OH primarily decomposes into H\(_2\) and CO as synthesis gas (c.f. Equation (3)). Additionally, as per the methanation reaction (c.f. Equation (4)), CO and H\(_2\) react with each other to produce steam that further converts into H\(_2\) and CO\(_2\) (c.f. Equation (5)). The produced CO\(_2\) assists in the fractional regeneration of the material by converting the C into CO (c.f. Equation (6)). Hence, along with TCD, a fractional cycle of regeneration also occurred that kept the surface of Ni fresh of CH\(_4\) dissociation.

Although it can be seen in the BET analysis that the incorporation of the Cu in Ni/Al\(_2\)O\(_3\) decreased the surface area of the material, the performance of the catalyst showed that the CH\(_4\) conversions and catalyst stability improved. The results show that the TCD of CH\(_4\) primarily depends upon the availability and dispersion of active sites on the catalyst support that overcomes the surface area deficiencies [45]. The effects of TCD temperature on the performance of the promoted catalysts with Cu over a range of 950–1100 K, evaluated as methane conversions, are shown in Figure 5. The conversions increased from 58% to 73% by increasing the reaction temperature from 973–1073 K due to the endothermic nature of the reaction. It was discovered that TCD is a temperature-dependent process, and the appropriate temperatures significantly affect the reaction yield. The study of thermocatalytic decomposition of methane over premixed gas feedstock has not yet been explored much. The motivation of the current study was researchers employing various hydrocarbons as feedstock together with methane, obtaining some promising results. The authors explained that the activity of the carbon obtained as a by-product seemed to affect the kinetics of the process as they used propane, ethylene, ethanol, and acetylene over a carbonaceous catalyst, and reasonable conversions were obtained. Moreover, the results depicted that the activity of carbon obtained as a by-product of benzene was highest, followed by ethylene, propane, and methane [27]. Thus, we carried out the study using premixed gas over metallic catalysts as the results were quite promising. Still, some extra work needs to be conducted in this research field, where the reaction parameters and reaction mechanism need to be further explored.
recent work (c.f. Figures 4 and 5). The formation of mixed oxides during calcination of
Figure 4. The effect of TCD temperature on methane conversions (973–1073 K, 1 bar, gas velocity
18 K mL g\(^{-1}\) h\(^{-1}\)).

3.3. Post Reaction Analysis of Spent Catalyst
3.3.1. Morphology Analysis

The formation and arrangement of coke deposited on the surface of both materials
tested for TCD of the methanol/methane mixture are shown in Figure 6. The hierarchy of
the carbon nanofiber produced as a by-product of TCD is dependent on the composition of
the metal in the catalyst. The morphology of the carbon encapsulated on both catalysts
varied in shape and size. It can be observed in Figure 6 that both graphene carbon
(GC) and carbon nanofibers (CNFs) having no distinct shape, but rather various shapes
(straight, zigzag, curved, and interwoven) are produced as a by-product of the catalytic
decomposition of feedstock. Wider CNFs were observed on the surface of the Cu-promoted
catalyst due to agglomerated particles and tip and base growth mechanisms. It can be
easily compared in the FESEM images that the morphology of the carbon produced as
a by-product improved, as wider CNFs in excess were deposited on the surface of the
Cu-promoted catalyst compared with Ni/Al\(_2\)O\(_3\).

![Figure 5](image_url)

**Figure 5.** The effect of TCD temperature on methane conversions (973–1073 K, 1 bar, gas velocity
18 K mL g\(^{-1}\) h\(^{-1}\)).

![Figure 6](image_url)

**Figure 6.** FESEM images of carbon deposited on the catalyst.
Moreover, the catalytic activity of Cat-2 was better and remained active for 6 h TOS. This finding shows that although carbon was produced, it did not block the active sites of the catalyst; instead, they acted as catalyst support. This finding is per the study by [39], where the authors reported that after successful impregnation of the metallic promoter on Ni-based catalyst, wider CNFs were produced that acted as catalyst support, improving the stability.

3.3.2. TEM Images

The nature of the carbon deposited on the surface of Cat-2 was examined by TEM images, as shown in Figure 7, over the TCD of 2% CH$_3$OH/CH$_4$ mixture at 1023 K. It can be observed in Figure 7 that both amorphous and crystalline forms of coke formed on the surface of Cat-2. Moreover, the carbon growth mechanism can also be studied by carefully analyzing the TEM images. The black dots in the CNF show the presence of Ni, both on the tip and in the body of the fiber. It was reported that the formation of CNF follows tip growth and base growth mechanisms [46]. In the present study, some of the Ni particles disconnected from the support, and they remained on the tip of CNF, therefore assisting in CH$_4$ dissociations. Additionally, some of the metal can be observed in the CNF body that helped in the growth of carbon nanofibers and multi-wall carbon nanofibers. Hence, we concluded that the carbon formation during the TCD of CH$_3$OH/CH$_4$ occurred simultaneously by tip and base growth mechanisms, as shown in Figure 7 [47].

![Figure 7. TEM images of carbon deposited on the catalyst.](image)

3.3.3. Raman Spectroscopy

The notch of crystallization and graphitization of the coke deposited over the Cu-promoted Cat-2 catalyst is shown in Figure 8 by Raman spectroscopy. The results show the existence of two characteristic bands, D and G bands, located at 1360 and 1527 cm$^{-1}$, respectively. The G band indicates the existence of highly ordered carbon structures, while the D band shows the defective structures of carbon originated as a by-product of TCD [48]. The ID/IG ratio over Cat-2 is estimated to be 1.0, which shows the presence of crystalline carbon as a by-product of TCD. The presence of both bands shows the existence of amorphous and crystalline carbon on the surface of the Cu-promoted catalyst. The vital difference between the relative intensities of both the D and G bands confirms the minor imperfections in the structure of carbon (c.f. Figure 8).
4. Conclusions

Catalytic decomposition of methane is an attractive technique for the production of clean hydrogen and carbon nanofiber (CNF), but high reaction temperature and rapid catalyst deactivation limit its industrial applications. In this research work, we attempted to optimize the reaction by employing 2% methanol premixed in methane as feedstock, and by running the reaction over Cu-promoted Ni-based metallic catalysts in a fixed-bed catalytic reactor. The materials were synthesized by the wet impregnation method, and characterized by TPR, XRD, BET, FESEM, TEM, and Raman spectroscopy. The results showed that due to the impregnation of metal on the support, the surface area was reduced due to the agglomeration of particles and the blockage of alumina pores, as confirmed by BET and FESEM analyses. Similarly, the reducibility of the catalyst was enhanced by impregnating Cu as the TPR profiles shifted to a lower temperature, with Ni° and Cu° being the outcomes of H₂ activation of both catalysts. The catalytic activity of Cat-2 significantly improved due to the presence of metallic Cu, and the conversions further increased by increasing reaction temperature. The post-reaction analysis of the spent carbon confirmed GF, CNF, and MWCNF. Although the addition of methanol improved the TCD process and the early deactivation of the catalyst was stopped, extra research work is needed to elaborate the reaction mechanism of the conversion of mixed-gas feedstock. In the future, various compositions of premixed gas feedstock should be tested for TCD for hydrogen production over bi-metallic catalyst, so that the process can be optimized.

Author Contributions: Conceptualization, A.A. and I.A.; methodology, A.A.; formal analysis, D.Q.; investigation, A.I.; resources, A.I.; data curation, D.Q.; writing—original draft preparation, A.A.; writing—review and editing, A.I.; visualization, M.S.K.; supervision, M.S.K.; project administration, I.A.; funding acquisition, A.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to acknowledge Karlstad University and Universiti Teknologi PETRONAS for providing the support and necessary facilities to conduct the research work.

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

1. Huff, C.; Long, J.M.; Abdel-Fattah, T.M. Beta-Cyclodextrin-Assisted Synthesis of Silver Nanoparticle Network and Its Application in a Hydrogen Generation Reaction. *Catalysts* 2020, 10, 1014. [CrossRef]

2. Punase, K.D.; Rao, N.; Vijay, P. A review on mechanistic kinetic models of ethanol steam reforming for hydrogen production using a fixed bed reactor. *Chem. Pap.* 2019, 73, 1027–1042. [CrossRef]

3. Chagas, C.A.; Manfro, R.L.; Toniolo, F.S. Production of Hydrogen by Steam Reforming of Ethanol over Pd-Promoted Ni/SiO₂ Catalyst. *Catal. Lett.* 2020, 150, 3424–3436. [CrossRef]

4. Chen, L.; Qi, Z.; Zhang, S.; Su, J.; Somorjai, G.A. Catalytic hydrogen production from methane: A review on recent progress and prospect. *Catalysts* 2020, 10, 858. [CrossRef]

5. Fakeeha, A.; Ibrahim, A.A.; Aljuraywi, H.; Alqahtani, Y.; Alkhodair, A.; Alsaidwan, S.; Abasaeeed, A.E.; Kasim, S.O.; Mahmud, S.; Al-Fatesh, A.S. Hydrogen Production by Partial Oxidation Reforming of Methane over Ni Catalysts Supported on High and Low Surface Area Alumina and Zirconia. *Processes* 2020, 8, 499. [CrossRef]

6. Ergazieva, G.E.; Telbayeva, M.M.; Popova, A.N.; Ismagilov, Z.R.; Dossumov, K.; Myltykbayeva, L.K.; Dodonov, V.G.; Sozinov, S.A.; Niya.zbayeva, A.I. Effect of preparation method on the activity of bimetallic Ni-Co/Al₂O₃ catalysts for dry reforming of methane. *Chem. Pap.* 2021, 1–10. [CrossRef]

7. Sisáková, K.; Oríňák, A.; Oríňáková, R.; Strečková, M.; Patera, J.; Welle, A.; Kostecká, Z.; Gírman, V. Methane Decomposition Over Modified Carbon Fibers as Effective Catalysts for Hydrogen Production. *Catal. Lett.* 2020, 150, 781–793. [CrossRef]

8. Ojelade, O.A.; Zaman, S.F. Ammonia decomposition for hydrogen production: A thermodynamic study. *Chem. Pap.* 2021, 75, 57–65. [CrossRef]

9. Lamacz, A.; Jagódká, P.; Stawowy, M.; Matus, K. Dry Reforming of Methane over CNT-Supported CeZrO₂, Ni and Ni-CeZrO₂ Catalysts. *Catalysts* 2020, 10, 741. [CrossRef]

10. Muhammad, A.F.A.S.; Awad, A.; Saidur, R.; Masiran, N.; Salam, A.; Abdullah, B. Recent advances in cleaner hydrogen productions via thermo-catalytic decomposition of methane: Amixture with hydrocarbon. *Int. J. Hydrogen Energy* 2018, 43, 18713–18734. [CrossRef]

11. Al-Mubaddel, F.; Kasim, S.; Ibrahim, A.A.; Al-Awadi, A.S.; Fakeeha, A.H.; Al-Fatesh, A.S. H₂ Production from Catalytic Methane Decomposition Using Fe-x-ZrO₂ and Fe-Ni/(x-ZrO₂)(x = 0, La₂O₃, WO₃) Catalysts. *Catalysts* 2020, 10, 793. [CrossRef]

12. Sivakumar, V.; Mohamed, A.; Abdullah, A.; Chai, S.P. Influence of a Fe/activated carbon catalyst and reaction parameters on methane decomposition during the synthesis of carbon nanotubes. *Chem. Pap.* 2010, 64, 799–805. [CrossRef]

13. Mei, I.L.S.; Lock, S.S.M.; Vo, D.V.N.; Abdullabh, B. Thermo-Catalytic Methane Decomposition for Hydrogen Production: Effect of Palladium Promoter on Ni-based Catalysts. *Bull. Chem. React. Eng. Catal.* 2016, 11, 191–199. [CrossRef]

14. Bayat, N.; Rezaei, M.; Meshkani, F. COx-free hydrogen and carbon nanofibers production by methane decomposition over nickel-alumina catalysts. *Korean J. Chem. Eng.* 2016, 33, 490–499. [CrossRef]

15. Shiraz, M.H.A.; Rezaei, M.; Meshkani, F. The effect of promoters on the CO₂ reforming activity and coke formation of nanocrystalline Ni/Al₂O₃ catalysts prepared by microemulsion method. *Korean J. Chem. Eng.* 2016, 33, 3359–3366. [CrossRef]

16. Al-Fatesh, A.S.; Amin, A.; Ibrahim, A.A.; Khan, W.U.; Soliman, M.A.; Al-Otaibi, R.L.; Fakeeha, A.H. Effect of Ce and Co addition to Fe/x-ZrO₂ Catalysts. *Catalysts* 2016, 6, 40. [CrossRef]

17. Ashik, U.; WAdua, W.; Abbas, H.F. Production of greenhouse gas free hydrogen by thermocatalytic decomposition of methane—A review. *Renew. Sustain. Energy Rev.* 2015, 44, 221–256. [CrossRef]

18. Kim, H.; Lee, Y.H.; Lee, H.; Seo, J.C.; Lee, K. Effect of Mg Contents on Catalytic Activity and Coke Formation of Mesoporous Ni/Mg-Aluminate Spinel Catalyst for Steam Methane Reforming. *Catalysts* 2020, 10, 828. [CrossRef]

19. Ashik, U.; Daud, W.W.; Hayashi, J.-I. A review on methane transformation to hydrogen and nanocarbon: Relevance of catalyst characteristics and experimental parameters on yield. *Renew. Sustain. Energy Rev.* 2017, 76, 743–767. [CrossRef]

20. Byun, M.Y.; Kim, J.S.; Park, D.W.; Lee, M.S. Influence of calcination temperature on the structure and properties of Al₂O₃ as support for Pd catalyst. *Korean J. Chem. Eng.* 2018, 35, 1083–1088. [CrossRef]

21. Wei, Y.; Li, S.; Jing, J.; Yang, M.; Jiang, C.; Chu, W. Synthesis of Cu–Co Catalysts for Methanol Decomposition to Hydrogen Production via Deposition–Precipitation with Urea Method. *Catal. Lett.* 2019, 149, 2671–2682. [CrossRef]

22. Awadallah, A.E.; Aboul-Enein, A.A.; Azab, M.A.; Abdel-Monem, Y.K. Influence of Mo or Cu doping in Fe/MgO catalyst for synthesis of single-walled carbon nanotubes by catalytic chemical vapor deposition of methane. *Fuller. Nanotub. Carbon Nanostruct.* 2017, 25, 256–264. [CrossRef]

23. Malaika, A.; Kozlowski, M. Hydrogen production by propylene-assisted decomposition of methane over activated carbon catalysts. *Int. J. Hydrogen Energy* 2010, 35, 10302–10310. [CrossRef]

24. Pinilla, J.L.; Suelves, I.; Lázaro, M.J.; Moliner, R. Influence on hydrogen production of the minor components of natural gas during its decomposition using carbonaceous catalysts. *J. Power Sources* 2009, 192, 100–106. [CrossRef]

25. Awad, A.; Salam, A.; Abdullabh, B. Thermocatalytic decomposition of methanemethanol mixture for hydrogen production: Effect of nickel loadings on alumina support. In *AIP Conference Proceedings*; AIP Publishing: New York, NY, USA, 2017.

26. Awad, A.; Salam, A.; Abdullabh, B. Hydrogen Production by Decomposition of Methane and Methanol Mixture over Ni-Pd/Al₂O₃. *Jpn. Inst. Energy* 2017, 96, 445–450. [CrossRef]

27. Awad, A.; Masiran, N.; Salam, M.A.; Vo, D.V.N.; Abdullabh, B. Non-oxidative decomposition of methanemethanol mixture over mesoporous Ni-Cu/Al₂O₃ Co-doped catalysts. *Int. J. Hydrogen Energy* 2018, 44, 20889–20899. [CrossRef]
28. Awad, A.; Salam, M.A.; Vo, D.V.N.; Abdullah, B. Hydrogen production via thermocatalytic decomposition of methane over Ni-Cu-Pd/Al2O3 catalysts. In IOP Conference Series: Materials Science and Engineering; IOP Publishing: Bristol, UK, 2020, pp. 1–7.
29. Awad, A.; Alnarabiji, M.S.; Salam, M.A.; Vo, D.V.N.; Setiabudi, H.D.; Abdullah, B. Synthesis, Characterisation, and Performance Evaluation of Promoted Ni-Based Catalysts for Thermocatalytic Decomposition of Methane. *ChemistrySelect* **2020**, *5*, 11471–11482. [CrossRef]
30. Thyssen, V.V.; Maia, T.A.; Assaf, E.M. Cu and Ni Catalysts supported on γ-Al2O3 and SiO2 assessed in glycerol steam reforming reaction. *J. Braz. Chem. Soc.* **2015**, *26*, 22–31.
31. Echegoyen, Y.; Suelves, I.; Lázaro, M.J.; Moliner, R.; Palacios, J.M. Hydrogen production by thermocatalytic decomposition of methane over Ni-Al and Ni-Cu-Al catalysts: Effect of calcination temperature. *J. Power Sources* **2007**, *169*, 150–157. [CrossRef]
32. Bayat, N.; Rezaei, M.; Meshkani, F. Methane dissociation to COx-free hydrogen and carbon nanofiber over Ni-Cu/Al2O3 catalysts. *Fuel* **2017**, *195*, 88–96. [CrossRef]
33. Bahari, M.B.; Phuc, N.H.H.; Abdullah, B.; Alenazey, F.; Vo, D.V.N. Ethanol dry reforming for syngas production over Ce-promoted Ni/Al2O3 catalyst. *J. Environ. Chem. Eng.* **2016**, *4*, 4830–4838. [CrossRef]
34. Bayat, N.; Meshkani, F.; Rezaei, M. Thermocatalytic decomposition of methane to COx-free hydrogen and carbon over Ni–Fe–Cu/Al2O3 catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 13039–13049. [CrossRef]
35. Bayat, N.; Rezaei, M.; Meshkani, F. Hydrogen and carbon nanofibers synthesis by methane decomposition over Ni–Pd/Al2O3 catalyst. *Int. J. Hydrogen Energy* **2016**, *41*, 5494–5503. [CrossRef]
36. Rastegarpanah, A.; Meshkani, F.; Rezaei, M. COx-free hydrogen and carbon nanofibers production by thermocatalytic decomposition of methane over mesoporous MgO-Al2O3 nanopowder-supported nickel catalysts. *Fuel Process. Technol.* **2017**, *167*, 250–262. [CrossRef]
37. Khan, W.U.; Fakeeha, A.H.; Al-Fatesh, A.S.; Ibrahim, A.A.; Abasaeed, A.E. La2O3 supported bimetallic catalysts for the production of hydrogen and carbon nanomaterials from methane. *Int. J. Hydrogen Energy* **2015**, *41*, 976–983. [CrossRef]
38. Chan, F.L.; Tanksale, A. Review of recent developments in Ni-based catalysts for biomass gasification. *Renew. Sustain. Energy Rev.* **2014**, *38*, 428–438. [CrossRef]
39. Bayat, N.; Rezaei, M.; Meshkani, F. Methane decomposition over Ni–Fe/Al2O3 catalysts for production of COx-free hydrogen and carbon nanofiber. *Int. J. Hydrogen Energy* **2016**, *41*, 1574–1584. [CrossRef]
40. Ashok, J.; Reddy, P.S.; Raju, G.; Subrahmanyan, M.; Venugopal, A. Catalytic decomposition of methane to hydrogen and carbon nanofibers over Ni–Cu–SiO2 catalysts. *Energy Fuels* **2008**, *22*, 5–13. [CrossRef]
41. Croy, J.R.; Mostafa, S.; Hickman, L.; Heinrich, H.; Cuenya, B.R. Bimetallic Pt-Metal catalysts for the decomposition of methanol: Effect of secondary metal on the oxidation state, activity, and selectivity of Pt. *Appl. Catal. A Gen.* **2008**, *350*, 207–216. [CrossRef]
42. Pambudi, N.A.; Laukkane, T.; Syamsiro, M.; Gandidi, I.M. Simulation of Jatropha curcas shell in gasifier for synthesis gas and hydrogen production. *J. Energy Inst.* **2017**, *90*, 672–679. [CrossRef]
43. Pinilla, J.L.; Suelves, I.; Utirila, R.; Gámez, M.E.; Lázaro, M.J.; Moliner, R. Hydrogen production by thermo-catalytic decomposition of methane: Regeneration of active carbons using CO2. *J. Power Sources* **2007**, *169*, 103–109. [CrossRef]
44. Abbas, H.F.; Daud, W.W. Thermocatalytic decomposition of methanol for hydrogen production using activated carbon catalyst: Regeneration and characterization studies. *Int. J. Hydrogen Energy* **2009**, *34*, 8034–8045. [CrossRef]
45. Awadallah, A.E.; Aboul-Enein, A.A.; Aboul-Gheit, A.K. Various nickel doping in commercial Ni–Mo/Al2O3 as catalysts for natural gas decomposition to COx-free hydrogen production. *Renew. Energy* **2013**, *57*, 671–678. [CrossRef]
46. Awadallah, A.E.; Aboul-Enein, A.A.; Aboul-Gheit, A.K. Effect of progressive Co loading on commercial Co–Mo/Al2O3 catalyst for natural gas decomposition to COx-free hydrogen production and carbon nanotubes. *Energy Convers. Manag.* **2014**, *77*, 143–151. [CrossRef]
47. Fakeeha, A.H.; Khan, W.U.; Al-Fatesh, A.S.; Ibrahim, A.A.; Abasaeed, A.E. Production of hydrogen from methane over lanthanum supported bimetallic catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 8193–8198. [CrossRef]
48. Pudukudy, M.; Yaakob, Z.; Mazuki, M.Z.; Takriff, M.S.; Jahaya, S.S. One-pot sol-gel synthesis of MgO nanoparticles supported nickel and iron catalysts for undiluted methane decomposition into COx free hydrogen and nanocarbon. *Appl. Catal. B Environ.* **2017**, *218*, 298–316. [CrossRef]