Hydrogen production via thermocatalytic decomposition of methane over Ni-Cu-Pd/Al₂O₃ catalysts

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Abstract. Non-oxidative decomposition of natural gas is a handsome technique for clean hydrogen production but high reaction temperature and rapid catalyst deactivation limitizes its applications. In current work, decomposition of methane into CO₅ free hydrogen and carbon nanofiber were studied over the bimetallic catalysts. The materials were prepared by wet impregnation method and analyzed by BET, TGA, XRD, FESEM, and TEM. It was observed that with an increase in the metal loading, the surface area was reduced but the methane conversions and catalyst stability were improved since the catalyst activity depend upon the active nickel sites that compensate the surface deficiencies. The highest conversion was given by Ni–Cu–Pd/Al₂O₃ (80%) over a period of 6 h despite having a low BET surface area (2.43 m² g⁻¹). The physiochemical properties reported that the synthesized catalyst possessed nanostructure and CNF were also produced along with hydrogen as products of TCD.

1. Introduction
The high concerns on the sustainability of environment due to the various effects of energy use in the form of global warming, depletion of ozone layer and acid rains has led to intense research on various forms of green fuels [1]. Hydrogen has been termed as an efficient and fuel of future [2]. Hence, major attention has been focused on the developing economic, environment-friendly and efficient approaches for hydrogen production [3]. Thermocatalytic Decomposition (TCD) has been termed as an attractive approach for producing pure hydrogen [4, 5]. The thermodynamic study of the process depicts that it is highly endothermic having 74.52 kJ mol⁻¹ enthalpy and hence occurs at very high temperatures [6]. The metallic catalyst with different supports and promoters have been stated to lower down the reaction temperatures, but they often deactivate rapidly due to the deposition of low active carbon on the surface of the catalyst [7]. Hence, high reaction temperature and rapid catalyst deactivation due to the deposition of inactive carbon on the metallic active sites hinders its applications. Extensive work has been done in TCD so that the best catalyst and most optimized reaction conditions can be summed
Ni is the most active metal for TCD of methane. It is reported that Ni performs well even at relatively low temperatures due to its high reactivity and a rise in its efficiency is observed when other metals are impregnated on it. Hence, the study on bimetallic catalysts opens up a very interesting area to reduce the TCD temperatures and increase the stability of material.

The impregnation of Cu, Fe, and Pd on Ni/Al₂O₃ were explored for TCD. Apart from that, these promoters have larger affiliation with carbon, acting like carbon reservoirs and diffusing more carbon. Thus, Ni remains active for methane adsorption and catalyst deactivation time is improved.

Sushil and Manoj et al. studied the effectiveness of adding Cu and Pd on the Ni-based catalyst and concluded that the catalyst was very effective for TCD of methane and CNF were produced as a by-product. Lock et al. reported that the addition of Pd on Ni/Al₂O₃ improved the thermal and catalytic satibility of the catalyst and showed slower deactivation rate.

In the proposed study, the impact of Cu and Pd on efficiency of Ni/Al₂O₃ towards thermocatalytic decomposition of methane is investigated.

2. Materials and Method

2.1. Catalyst Synthesis
The catalysts 50%Ni/Al₂O₃ and 50%Ni−15%Cu−0.9%Pd/Al₂O₃ were synthesized by wet impregnation method. Stoichiometric amounts of the Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Pd(NO₃)₂·2H₂O, and γ-Al₂O₃ were employed in this work. The aqueous solutions of metal precursors were concurrently emptied on γ-Al₂O₃ support. The mixture was stirred at for 3 h at 400 rpm, dried at 383 K for 12 h and finally for 4 h it was calcined at 873 K. Lastly, it was crushed and labeled.

2.2. Catalyst Characterization
The catalyst was characterized by using thermogravimetric analysis using TGA 6200 (thermogravimetric analysis) to investigate the thermal behavior, weight loss, and structural analysis of the catalyst. The 0.01 g of catalyst treated under a nitrogen flow of 50 mL min⁻¹ was heated up to 1273 K at a heating rate of 10 Kmin⁻¹. The BET surface area measurements were determined using N₂ physisorption at 77 K by using Micromeritics ASAP 2020. Bruker D8 Advance (USA) X-ray diffractometer was used to record the powder X-ray Diffraction (XRD) spectra. 40 mA tube current with a scanning speed of 2° per minute between 10° and 90° 2θ Cu Kα1 radiation (λ=1.54 Å) at 40 kV tube voltage were employed. SUPRA 55VP manufactured in the Carl Zeiss AG, having acceleration voltage of 0.1−30 kV and magnification of 12−900,000 X was used to study the interfacial properties of fresh and spent catalyst. Transmission Electron Microscope (FETEM) of model number JEM-2100F, 200 kV and brand JEOL was finally used to see the morphology of carbon deposited on the surface of the post reaction catalyst.

2.3. Catalyst Evaluation
Thermocatalytic decomposition of methane was carried on fixed bed temperature controlled catalytic reactor. Approximately 0.1 g of finely sieved catalyst via quartz wool was placed in the center of the stainless tube of the reactor. Agilent 7820A series gas chromatography was used to evaluate the post reaction gases.

3. Results and Discussion

3.1. Analysis of fresh catalysts

3.1.1. Textural properties
The properties of 50%Ni/Al₂O₃ and 50%Ni−15%Cu−0.9%Pd/Al₂O₃ determined by BET show that the impregnation of Cu and Pd to 50%Ni/Al₂O₃ caused a decrease in surface area. It is observed that
50%Ni/Al$_2$O$_3$ possessed surface area of 5.15 m$^2$g$^{-1}$ that shrink to 2.43 m$^2$g$^{-1}$ in 50%Ni−15%Cu−0.9%Pd/Al$_2$O$_3$ catalyst. The decline in surface area and pore volume via increasing the metal loading can be principally attributed to decrease in the concentration of γ−Al$_2$O$_3$ which is a major contributor to the high surface properties and fractional filling of its pores by Cu and Pd oxides [19].

3.1.2. Thermogravimetric analysis
The TGA profiles of 50%Ni/Al$_2$O$_3$ and 50%Ni−15%Cu−0.9%Pd/Al$_2$O$_3$ as shown in figure 1 are employed to study the thermal stability of synthesized catalyst over 283−1200 K. The thermal decomposition of the nanoparticles occurred in two distinct steps, i.e., dehydration of moisture and formation of metal oxides through break down of metal nitrates each showing independent stages represented as zones 1–4 (cf. figure 1). The first two zones located at a temperature range of 320–500 K were assigned to the evaporation of moisture from the mesoporous structure of the catalyst and partial decomposition of the metal nitrates. The third zone stable beyond 673 K explain the complete conversion of Pd (NO$_3$)$_2$, Cu (NO$_3$)$_2$, and Ni (NO$_3$)$_2$ into PdO, CuO, and NiO, respectively.

![Figure 1. TGA analysis of fresh catalysts.](image)

3.1.3. X-Ray diffraction measurement
The XRD diffractograms of 50%Ni/Al$_2$O$_3$ and 50%Ni−15%Cu−0.9%Pd/Al$_2$O$_3$ (cf Figure2) are employed for phase identifications in the synthesized catalysts. The typical peaks of γ−Al$_2$O$_3$ at 2θ of 25°, 35°, 44°, 55°, 58°, and 66° were detected on both catalysts. It was observed that NiO was the only Ni containing active phase and was detected at 2θ of 37.4°, 64.3°, 75.3°, and 79° possessed by both the promoted and unpromoted catalyst. It was worth noting that in promoted catalyst Cu was found in the form of mixed oxides as Ni$_{1+2x}$Cu$_x$O and the peaks overlapped with that of NiO. The characteristic peaks at 55°, 73°, and 75° belonged to the presence of PdO phase in the catalyst [20].
Figure 2. XRD analysis of calcined catalysts.

3.1.4. Morphological analysis of fresh catalyst
The surface morphology of the calcined catalyst 50%Ni/Al₂O₃ and 50%Ni–15%Cu–0.9%Pd/Al₂O₃ at 873 K shows that both catalysts possess nanoparticles contained in large spongy clusters and it can be seen in figure 3 (a) and (b). The incorporation of active metal oxides on base catalyst decreased its porosity as empty voids of the support are filled in by Cu and Pd. It is observed that the particles of prompted catalyst are more uniform as compared to Ni/Al₂O₃. The particle size ranges from 25–200 nm.

Figure 3. FESEM images of pre-reaction catalysts
3.2. Thermocatalytic reaction Study

The performance of the synthesized catalysts 50%Ni/Al₂O₃ and 50%Ni–15%Cu–0.9%Pd/Al₂O₃ was evaluated for TCD of methane at 1023 K and GHSV of 18,000 mL g⁻¹cat h⁻¹ as shown in Figure 4. It was observed that the deactivation of 50% Ni/Al₂O₃ over a period of 4 h occurred in the current study resulting in 25% of methane conversion understated reaction parameters due to formation of ample amount of carbon and inability of unpromoted catalyst to diffuse it. The effect of promoting 50% Ni/Al₂O₃ with Cu (15%) and Pd (0.9%) is evident from Fig 4 that the catalytic activity has been improved from 25% to 80% and stability from 4 to 6 h by adding Cu and Pd on parent catalyst [21]. The presence of Cu enhances the catalytic efficiency as it has been proposed that graphene has a larger affinity with Cu which inhibits its encapsulation on the surface of Ni. Moreover, the dispersal of coke in Pd is cited to be six times faster than Fe, Ni or Co [22].

![Figure 4. TCD of CH₄ over time on stream over CH₄ as feedstock.](image)

3.3. Analysis of spent catalyst

3.3.1. FESEM analysis

The properties of numerous forms of coke produced on 50%Ni–15%Cu–0.9%Pd/Al₂O₃ operated at 1023 K are shown in figure 5. Carbon nanofibers with a diameter of few nanometers can be easily scrutinized deposited on the surface of the catalyst. The carbon nanofibers were formed in the interwoven hierarchy, making it nearly impossible to estimate the precise length and diameter of them. Moreover, these carbon fibers are observed to be long and entangled in shape with diverse diameters. Additionally, relatively wider CNF are seen deposited on 50%Ni–15%Cu–0.9%Pd/Al₂O₃ as compared to 50%Ni/Al₂O₃.
3.3.2. TEM analysis

The properties of carbon produced as result of TCD of methane via TEM is shown in Fig 6. It can be seen that irregular carbon having various dimensions is dumped on the surface of 50%Ni-15%Cu-0.9%Pd/Al2O3. The dark spots present in the tip and body of CNF confirm the presence of Ni on the tip and base of carbon fibers.

4. Conclusion

50%Ni/Al2O3 and 50%Ni-15%Cu-0.9%Pd/Al2O3 were produced by wet impregnation method. The former catalyst proved to be an active catalyst for non-oxidative breakdown of natural gas with 80% methane conversions at 1023 K and 18,000 ml gcat⁻¹h⁻¹. The catalyst produced CNF with 25–200 nm diameter. The FESEM analysis also discovered that the basic appearances of CNF were influenced by the adding of Cu and Pd promoters on Ni/Al2O3. Moreover, the promoted catalyst gave uniform conversions over a course of 6 h. Cu and Pd the tendency to promote the dispersion of Ni on alumina and increase the dispersion rate of carbon which facilitates the catalyst performance.

5. References

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