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Hydrogen Production by Decomposition of Methane and Methanol Mixture over Ni-Pd/Al₂O₃

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Thermocatalytic decomposition of methane (TCD) is a promising method for producing hydrogen. However, the main concerns of this process are very high reaction temperature and fast deactivation of the catalyst. In this work, a positive approach has been made to minimize both effects by using Pd-promoted catalyst prepared by the co-precipitation and impregnation method. Pd has a high affiliation with carbon, thus instead of encapsulating Ni, it diffuses in promoter hence the catalytic lifetime is prolonged. EDX and XRD analysis confirmed the presence of NiAl₂O₄, Al₂O₃, Pd, and Ni. BET analysis depicts that the surface area is decreased as the amount of metal content impregnated on the support is increased. FESEM analysis shows the nano particles are synthesized while carbon nanofibers are produced as by-product. The highest conversion of CH₄ was given by Cat 1 (24.7 wt%Ni-0.3 wt%Pd/Al₂O₃) i.e. 45%.

Key Words

TCD, Methane, Metal loading, Nano particles, CNF

1. Introduction

Hydrogen often recalled as the world lightest element has very high amount of energy stored in it and has many applications and uses. It is widely used in chemical mechanical to refineries, metallurgical, glass, and electronics. Apart from that, it is also a very clean fuel and an excellent alternative to the extensively used fossil fuels¹⁾. The major application of hydrogen includes its usage in proton exchange membrane fuel cells (PEMFC). Hydrogen energy and fuel cells are nowadays regarded as one of the vital energy solutions of this ongoing century²⁾. Secondly, the amount of energy produced by hydrogen is relatively higher than the combustion of any other fuel as on kg of hydrogen gives the same amount of energy as one gallon of gasoline³⁾.

Hydrogen cannot be obtained in the pure atomic state rather it is in the molecularly combined form with oxygen and carbon⁴⁾. There are many processes for hydrogen production i.e. dry reforming, steam reforming, auto-

thermal reforming, partial oxidation and water electrolysis. However, all these processes require a large amount of energy, produce a significant amount of carbon dioxides and carbon monoxides, and the quality of hydrogen is not good as the large amount of capital as well as equipment is required to extract the hydrogen from CO_x mixtures^{5)~11)}. The recent research that methane can be directly decomposed into pure hydrogen and carbon nanotubes by a process i.e. thermocatalytic decomposition of methane (TCD) has gained much interest among researchers, and a significant amount of work has been underway in this area. The equation of reaction is shown as^{12) 13)}.

The thermocatalytic decomposition results in the production of gaseous hydrogen and filamentous carbon as the dissociation of methane occurs on the surface of the catalyst¹⁴⁾. The carbon obtained has many applications both domestically and industrially due to high mechanical strength, high resistant behavior against strong acids and bases and high electron negativity. So being the most effective and purest hydrogen production method, lack of carbon oxides production, high-quality carbon as a byproduct and environment-friendly behavior TCD can be used an alternative to other hydrogen production methods

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stated above ^{15) ~ 17)}.

Although methane can be decomposed into hydrogen, yet a very high amount of energy is required. The reason behind that is an adamant bond between C-H. The use of different supports and promoters has been widely studied by the researchers so that the reaction temperature can be lowered, the hydrogen yield and catalyst deactivation time can also be improved ¹⁸⁾. The addition of supports and promoters increase the surface area of the catalyst, and the metallic particles finely dispersed on the surface of the support thus giving a homogenized surface for methane dissociation. Different types of supports like alumina, iron oxide, ceria, magnesium aluminates and lanthanum oxides are employed ^{19) ~ 21)}.

The use of Pd in the supported catalyst increases the catalyst deactivation time as Ni-Pd alloy is formed that performs well and has higher catalytic efficiency as compared to the catalytic performance of Ni and Pd independently. The Ni-Pd alloy absorbs a larger amount of carbon produced and thus avoids the accumulation of carbon on the surface of the catalyst as the methane dissociation continues on the surface of the active sites ^{22) 23)}. On the other hand, promoters like Cu also optimize the TCD as it prevents the agglomerations of the metallic particles on the surface of the support and helps the fine dispersion. Additionally, it prevents the deposition of carbon on the surface of the catalyst ²⁴⁾.

The co-feeding of methane with other hydrocarbons has been an attractive technique in incapacitating the problems of high reaction temperature and fast catalyst deactivation of TCD. The reactivity of carbon produced from other hydrocarbons is high thus instead of encapsulating the active sites of the catalyst they act as a catalyst. The order of activity of carbon of various hydrocarbons in of the order as $C_{\text{benzene}} > C_{\text{acetylene}} > C_{\text{ethylene}} > C_{\text{propane}}$ and C_{methane} ²⁵⁾. Little work has been done on co-feeding of methane with other hydrocarbons to stabilize the catalyst activity and deactivation time. The mostly studied hydrocarbons are ethane ²⁶⁾, ethylene ^{27) 28)}, propylene ²⁵⁾, ethanol ^{29) 30)} and acetylene ³¹⁾. Apart from that CO_2 ³²⁾ and H_2S ³³⁾ are also used as co-feed with methane.

In this research work, an effective approach has been made by synthesizing Ni-Pd/ Al_2O_3 by co-precipitation and impregnation method and studying the effect of this catalyst on TCD of 2% methanol/methane mixture.

2. Experimental

2.1 Material Preparation

The catalyst was prepared by using both impregnation and co-precipitation method. Ni/ Al_2O_3

Table 1 Weight percentage of each composition of catalysts in designed formulations

S. No	Sample Name	Al_2O_3	Ni	Pd
1.	Cat 1	75%	24.7%	0.3%
2.	Cat 2	85%	14.7%	0.3%
3.	Cat 3	95%	04.7%	0.3%

was synthesized by using co-precipitation method. The stoichiometric amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in a beaker with constant stirring at 60 °C. 5% NH_3 solution was added dropwise so that the pH can be controlled to 9. After obtaining the desired pH, the temperature was increased to 90 °C, and the solution was stirred for 1 h. After that, the solution was filtered and then washed several times with deionized H_2O so that the traces of NH_3 can be removed completely. The stoichiometric amount of dichloro Pd was then impregnated on the Ni/ Al_2O_3 catalyst prepared by the co-precipitation method. Once the catalyst was synthesized, it was dried overnight at 110 °C and then calcined at 600 °C for 4 h. The samples were termed as in **Table 1**.

2.2 Material Characterization

The characterization of the catalyst has been done by using EDX, BET, XRD and FESEM analysis. The textural properties of the materials were studied by nitrogen adsorption-desorption technique using a micromeritics ASAP 2020 sorptometer. The elemental analysis was given by the Energy Dispersive X-Ray Spectroscopy (EDX). Surface morphology of the samples was studied by using field-emission scanning electron microscope (FESEM) from CARL Zeiss Supra 55VP instrument equipped with the Oxford INCA 400 EDX microanalysis system.

2.3 Material Evaluation

A high temperature catalytic fixed bed reactor (Model No: GT1000) was used for thermocatalytic decomposition of methane. For each run of experiment 0.5 g of catalyst was finely sieved and was charged in the tube of the reactor. The gaseous feedstock 2% methanol methane mixture 40 sccm and the nitrogen 50 sccm were introduced into the reactor controlled by the auto flow meters. Nitrogen was used as a carrier gas. Before this, the catalyst was reduced at hydrogen flow rate of 50 sccm at 600 °C for 2 h, and then the required reaction temperature was obtained. Gaseous products were analyzed by Agilent 7820A Series gas chromatography equipped with both thermal conductivity (TCD) and flame ionization (FID) detector. The schematic rig of experimental setup is shown in **Fig. 1**.

Fig. 1 Schematic Rig of Experimental Setup

3. Results and Discussion

3.1 Elemental Analysis (EDX)

The composition of the catalyst was obtained by Energy Dispersive X-Ray Spectroscopy. The EDX graphs of Cat 1-3 are shown in Fig. 2. The results confirm the presence of Ni, Pd and Al_2O_3 in their actual atomic weight compositions. Cat 1 shows the highest amount of Ni i.e. 24.7%, followed by Cat 2 with Ni content as 14.7%, and Cat 3 Ni 4.7%. The amount of Pd is the same in all the catalyst that has been confirmed by the EDX analysis³⁴⁾³⁵⁾.

3.2 Textural Analysis (BET)

Table 2 summarizes the textural properties of Cat. 1-3. Al_2O_3 shows relatively higher surface area and pore volume which is the reason behind the fine dispersion of Ni and Pd on the surface of the catalyst. The addition of Ni and Pd decreased the surface area and the pore volume.

The reduction in surface area is due to the partial blockage of Al_2O_3 pores as well as the agglomeration of metal particles³⁶⁾.

3.3 Morphological Analysis (FESEM) of Fresh Catalyst

The morphological analysis of Ni/ Al_2O_3 and Ni-Pd/ Al_2O_3 has been explained in Fig. 3 (a) and (b) respectively. The surface morphology of the metallic catalyst mainly depends upon the synthesis conditions i.e. temperature, pH and the method used and the chemical compositions.

Table 2 Structural analysis of catalysts

S. No	Sample	BET S.A m^2/g	Langmuir S.A m^2/g	Pore Vol cm^3/g
1.	Cat 1	73.6	112.2	0.07
2.	Cat 2	77.0	116.8	0.09
3.	Cat 3	230.5	353.4	0.29

Fig. 2 EDX Analysis (a) Cat#1 (b) Cat#2 (c) Cat#3

Fig. 3 FESEM Analysis of Fresh Catalyst (a) Ni/Al₂O₃ (b) Ni-Pd/Al₂O₃

The agglomerated particles can be seen. The porosity decreased as the metals were incorporated on the surface of the supports. The catalysts surface are more uniform when Ni and Pd are incorporated on the catalyst. The Pd supported catalyst are more consistent in structure as compared to the Ni supported catalyst³⁷.

3.4 Structural Analysis (XRD)

The XRD analysis of Ni/Al₂O₃, Pd/Al₂O₃ and Ni-Pd/Al₂O₃ has been elaborated in Fig 4. As seen in in Fig. 4 (a) the diffraction peaks at 36°, 46°, 60° and 66° are related to in active NiAl₂O₄ species while on the other hand the peaks at 36°, 46° and 66° showed the presence of Al₂O₃. Pd-promoted on Al₂O₃ has been shown in Fig. 4 (b). Pd peaks appeared at 33°, 40°, 46° and 69° while the peaks at 36°, 46° and 66° proved the existence of Al₂O₃. It is noteworthy that inactive Al₂O₄ was not formed in this catalyst hence this catalyst performs well as compared to the Ni-based catalyst. Lastly, Fig. 4 (c) illustrates the structural analysis of Ni-Pd/Al₂O₃ catalyst. This sample demonstrated a unique profile which is a bit different to the one seen for mono metallic catalyst. The results confirm that the formation of Ni-Pd alloy that is the responsible for increasing the methane

Fig. 4 XRD analysis (a) Ni/Al₂O₃ (b) Pd/Al₂O₃ (c) Ni-Pd/Al₂O₃ Reproduced with permission from Reference 38), copyright 2016 Indonesia Catalyst Society

conversion and adding to the catalyst activity³⁸.

3.5 Performance Evaluation

Methane decomposition is an endothermic reaction so requires intensive energy to break the bonds. The presence of a metallic catalyst with appropriate support favors the reaction as the reaction temperature and the catalyst deactivation time is optimized. The addition of Pd improves the catalyst stability as the carbon grows from several faces and hence the active sites of the catalyst are prevented from encapsulated carbon. Ni also forms an alloy with Pd as Ni-Pd which works better under specified conditions²². The methane conversions increased as the metal loadings were increased. The highest conversion was given by Cat 1 i.e. 45%, and the catalyst was stable for 4 h. Methanol decomposes at lower temperatures, hence at 550 100% methanol was decomposed. The methane conversions of Cat 1-3 are summarized in Fig. 5.

The efficiency of Cat 1 was compared to the 30%Ni/Al₂O₃ for the decomposition of 2% methanol/methane mixture for the same set of conditions is given in Fig. 6.

Fig. 5 Methane conversions at 550 °C

Fig. 6 Comparison of methane conversions over Cat 1 and 30 wt% Ni/Al₂O₃

The former catalyst gave better conversions as compared to the latter one as methane conversion was decreased from 45% to 25% while the conversion of methanol in both cases was cent percent. This adds to the discussion that addition of Pd has a positive effect on the catalyst stability and activity. Lastly, the hydrogen obtained as the result of TCD of 2% methanol/methane by Cat 1 has given in Fig. 7. As already elaborated, methanol was completely decomposed. The conversion provided by Cat 1 was almost 45% correspondingly giving a uniform hydrogen of 21%. It has been explained by equation 2 that TCD of methane provides pure hydrogen as well as elemental carbon as by-product. Hence gaseous hydrogen was detected by GC and carbon in the form of CNF was deposited on the surface of the catalyst.

The conversion is obtained by Equation (2):

$$\text{Methane Conversion} = \frac{\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out}}{\text{CH}_4 \text{ in}} \times 100 \quad (2)$$

Fig. 7 Methane conversions and hydrogen % at 550 °C by Cat 1

3.6 Morphological Analysis (FESEM) of Spent Catalyst

Fig. 8 shows the FESEM analysis of spent catalyst for Ni/Al₂O₃ and Ni-Pd/Al₂O₃. The images are in support of the formation of filamentous carbon. The diameter and length of these CNF ranges in a few nano meters. The interwoven nature of these CNF makes it extremely difficult to predict the exact diameter and length. The dimensions of Pd-promoted catalyst are better as compared to Ni promoter catalyst³⁷.

4. Conclusion

In this research work, the effects of Pd supported on Ni/Al₂O₃ and 2% methanol/methane mixture have been studied for TCD of methane. Ni has always proved to be an active metal and impregnating Pd as promoter makes an alloy that increases the methane conversion as well as works against catalyst deactivation. The results show that Ni-Pd alloy has been formed. Pd has a high affiliation

Fig. 8 FESEM Analysis of Spent Catalyst (a) Ni/Al₂O₃ (b) Ni-Pd/Al₂O₃

with carbon, thus instead of encapsulating Ni, it diffuses in promoter thus the catalytic life time is prolonged. The best activity was given by Cat 1. The results were compared with 30%Ni/Al₂O₃, and it was perceived that addition of Pd has a positive impact on TCD. 2% methanol, on the other hand, was completely decomposed. FESEM results revealed that CNF were produced as by-product.

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