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Production of Hydrogen via Thermocatalytic Decomposition of Methane using Ni/ZnO catalyst

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Abstract—***Thermo Catalytic Decomposition of Methane (TCD) is a promising method to produce COx free hydrogen and carbon. In this study, Nickel supported on zinc oxide (Ni/ZnO) catalyst for the hydrogen production through thermo catalytic decomposition of methane were reported. The effect of Ni weight percentage (10%, 20%, 30% and 40wt %) and reaction temperature (650, 700, 750 and 800ºC) with ZnO catalyst was performed for hydrogen production studies at 54sccm flowrate of methane. It was observed that at 30wt% Ni/ZnO catalyst showed the maximum hydrogen production of 34.54 volume% respectively at 60min of reaction time and temperature of 700ºC. Before and after hydrogen production studies, catalysts were characterized by XRD, BET surface area, SEM and TEM analysis. Apart from hydrogen production, carbon nanorods were observed with a diameter of 5-10nm and length is found to be around 0.4µm for Ni/ZnO catalysts.***

Keywords: Hydrogen; Nickel supported on zinc oxide (Ni/ZnO); Thermo Catalytic Decomposition.

I. INTRODUCTION

Hydrogen is an alternative fuel because of its eco-friendly nature [1] that can be produced from domestic resources. Several methods of hydrogen production are known [2]. Presently, the most familiar conventional methods for hydrogen production are steam methane reforming and methane partial oxidation. These methods produce a huge quantity of carbon oxides along with hydrogen, which creates massive environmental troubles. Further, carbon oxides are poison for the catalysts used for the ammonia synthesis, hydrogenation process and fuel cells [3-6]. Thermo catalytic decomposition (TCD) of methane is measured as a striking alternative method as a substitute of the conventional methods for hydrogen production with a high purity [7]. It does not require any complicated processes to remove carbon oxides, which makes the method simple and reduces the price of production [8]. The most active metals in TCD were Ni, Co and Fe and extensive studies were performed [7, 9]. Nickel is the most active metal for thermo catalytic decomposition of methane to hydrogen and carbon nanomaterials. Ni-based catalysts were extensively studied for methane decomposition due to their higher activities compared with other transition metals [10- 12]. Till now to our best knowledge, no one was reported on Nickel supported ZnO catalyst. In this study, an attempt made using Ni/ZnO catalyst for the hydrogen production. Ni/ZnO catalyst for hydrogen production using thermocatalytic decomposition of methane. The different reaction conditions such as Ni weight percentage (10%, 20%, 30% and 40wt %) and reaction temperature (650, 700, 750 and 800ºC) were performed for hydrogen production studies at 54sccm flow rate of methane.

II. EXPERIMENTAL PREPARATION OF NICKEL SUPPORTED ZINC OXIDE CATALYST

An auto combustion method has been adopted for synthesizing Nickel supported zinc oxide catalyst. 0.1M of Nickel nitrate hexahydrate dissolved in distilled water in one beaker, and in another beaker zinc nitrate is dissolved in distilled water. Then both the solutions were mixed and stirred well in a magnetic stirrer for 20min and then fuel (1.36g Glycine) is added to above solution. Then the beaker is kept on hot plate to complete the combustion at 300ºC for 5-10min. Then the sample is calcined at 550ºC for 1hr to obtain Ni/ZnO catalyst [13]. Thus formed catalyst is Nickel supported zinc oxide catalyst. The synthesis of Nickel supported zinc oxide catalyst is shown in Flow chart-1.

A. Experimental set up

Thermo catalytic decomposition of methane studies were carried out in an indigenously fabricated conventional gas flow fixed bed reactor system comprising a reactor of internal diameter 16 mm and heating zone length of 250 mm. The detail of the experimental set up was given in previous published paper [14].

Flow chart-1 Synthesis of Nickel supported Zinc Oxide catalyst

B. Experimental procedure

2.5g of Ni/ZnO catalyst were used. Experiments were carried out at atmospheric pressure. Weight percentage of Ni at 10, 20, 30 and 40 wt% were evaluated for ZnO support at different reaction temperatures 650-800ºC. The gas samples were collected in TeddlarTM bags. Hydrogen collected in TeddlarTM bags were analyzed using Agilent 6890 gas chromatograph (TCD detector, nitrogen as carrier gas and Gaspro column, Oven temperature: 120°C). Chemstation was used for the interpretation of gas chromatograph data.

C. Characterization Studies

X-ray Diffraction (XRD) patterns of catalysts were analyzed using a Bruker D8 Advanced X-ray Diffractometer operating at 40kV and 30mA with Cu Kα radiation (λ=0.154nm) between 2θ diffraction angles (20°-80°). The surface analysis of catalysts before and after hydrogen production studies with BET Micromeritics 2010 model. The surface morphology of catalysts before and after hydrogen production studies were analyzed using Scanning electron micrograph (SEM) with Hitachi S – 3700 Super (SEM) operating at an accelerating voltage of 15 kV. The surface morphology of samples before and after hydrogen production studies were analyzed using JEOL JEM-2100 Transmission electron microscopy (TEM).

III. RESULTS AND DISCUSSION

The hydrogen production studies of Ni/ZnO catalyst were carried out by varying nickel weight percentage, reaction temperature and reaction time.

A. Effect of nickel weight percentage and reaction temperature

The effect of nickel weight percentage and reaction temperature in Ni/ZnO catalyst for hydrogen production studies at constant flowrate of methane as 54sccm. The obtained hydrogen production from Ni/ZnO catalyst was shown in Table-1. The Nickel loading on ZnO was varied from 10 to 40 wt%. The maximum hydrogen production of 34.5 volume % at 30 wt% was observed at 60min of reaction time at 700ºC. Increasing the Ni wt% at 10%, 20%, 30% and 40 wt%, the hydrogen production volume % observed to be 7.3%, 12.4%, 34.5% and 10%. At the reaction temperatures of 650, 700, 750 and 800ºC, the hydrogen production volume % observed to be 11.2%, 34.5%, 10.1% and 5.5 % respectively. This is due to blockage of the active sites by the carbon deposits produced during the reaction. Therefore, a catalyst with 30wt%Ni/ZnO and 700ºC reaction temperature was investigated in the following experiment.

B. Effect of reaction time

The effect of reaction time in Ni30/ZnO catalyst studied for hydrogen production at 700ºC by maintaining constant flow rate of methane as 54sccm. The obtained hydrogen production of Ni30/ZnO catalyst is shown in below Fig.1. From Fig.1, it was observed that hydrogen production increased upto 34.54 Volume% in 60min of reaction time and then further it was decreased to 10.15 Volume% in 300min of reaction time and then catalyst deactivated at 360min. The catalyst activity decreased with the time, which points to a loss of activity due to blockage of the active sites by the carbon deposits produced during the reaction.

C. X-ray diffraction (XRD) Analysis of Ni30/ZnO catalyst

The XRD pattern of the Ni30/ZnO catalyst (Fig.2)before hydrogen production reaction showed intense peaks at the 2θ angles of ZnO (100) at 32°, ZnO (002) at 34°, Ni (111) and ZnO (101) at 36°, ZnO (102) and Ni (200) at 48°, ZnO(110) at 57°, Ni (220) and ZnO (103) at 62°, ZnO (201) at 68°, Ni (311) at 70° and Ni (222) at 78°, the average crystallite size was 20nm. The XRD data is referred with the Pdf-2 release ICDD database 2003.

The XRD pattern of the Ni30/ZnO catalyst (Fig.3) after hydrogen production reaction showed intense peaks at the 2θ angles of C (002) at 32°, ZnO (002) at 34°, Ni (111) at 37°, C(100) at 42°, Ni (200) and C (101) at 45°, ZnO (102) at 48°, C (004) and Ni (200) at 52°, ZnO (110) at 57°, Ni (220) at 62°, ZnO (201) at 68° and C (110) at 75°, the average crystallite size was 28nm. The XRD data is referred with the Pdf-2 release ICDD database 2003

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TABLE-1 EFFECT OF ICKEL WEIGHT PERCENTAGE AND REACTION TEMPERATURE ON HYDROGEN PRODUCTION WITH NI/ZNO CATALYST

Sample	Hydrogen Production (Volume %)			
	650°C	700°C	750°C	800°C
10wt%Ni/ZnO	3.54	7.35	3.12	2.51
20wt%Ni/ZnO	8.20	12.42	7.11	4.12
30wt%Ni/ZnO	11.25	34.54	10.14	5.50
40wt%Ni/ZnO	5.00	10.05	4.25	3.21

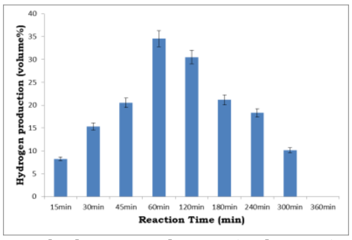

Fig.1 Effect of reaction time on hydrogen production (Volume %) with Ni30/ZnO catalyst

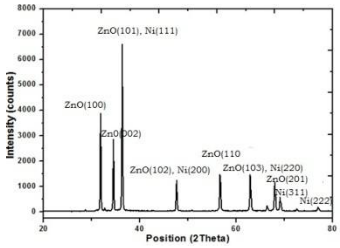

Fig.2 XRD plot of Ni30/ZnO catalyst before hydrogen production reaction

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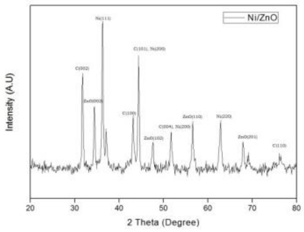

Fig.3 XRD plot of Ni30/ZnO catalyst after hydrogen production reaction

D. BET Surface area of Ni30/ZnO catalyst

The surface area, pore volume and average particle size of Ni30/ZnO catalyst were given in Table-2. The surface area and pore volume of Ni30/ZnO catalyst was decreased from 177.0 to 27.5m2/g and 0.15 to 0.05cm3/g, over a period of 360min of reaction time. This might be due to the formation of carbon particles deposition on the clear surface of the catalyst. Average particle size of Ni30/ZnO catalyst was observed to be 4.0 to 36.5nm from BET surface area analysis which states that the surface area decreases with increase in particle size. The loss in BET surface area leads to decrease in hydrogen production. From Table-2, we observed that Pore volume decreases with increase in average particle size. The carbon deposition over Ni catalyst is due to larger crystal size and the nature of ZnO effects surface area and pore volume.

After the hydrogen production reaction, decrease in surface area indicates that the larger pores were filled with the carbon deposits. Carbon deposits blocks the porosity, stopping the methane molecules from going access to the part of surface area of the carbon. As a result, catalyst activity decreases.

E. Scanning Electron Microscope (SEM) Analysis of Ni30/ZnO catalyst

The SEM images of Ni30/ZnO catalyst before and after reaction were shown in Fig.4; we observed that sample in amorphous nature before reaction and carbon nanorods were observed after reaction.

TABLE-2 SURFACE ANALYSIS OF NI30/ZNO CATALYST

Sample Code	BET Surface area, Before reaction (m^2/g)	BET Surface area, After reaction (m^2/g)	Total Pore volume Before reaction (cm^3/g)	Total Pore volume After reaction (cm^3/g)	Average Particle Size, Before reaction (nm)	Average Particle Size, After reaction (nm)
Ni_{30}/ZnO	177.0	27.5	0.15	0.05	4.0	36.5

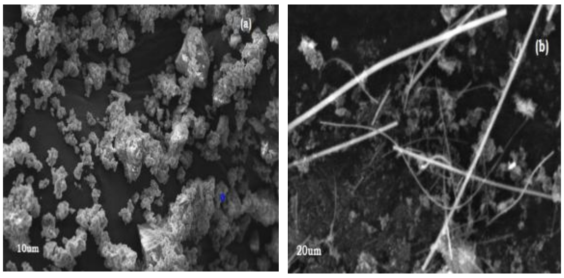

Fig.4 (a) SEM image of Ni30/ZnO catalyst before and (b) SEM image of Ni30/ZnO catalyst after hydrogen production reaction.

F. *Transmission Electron Microscopy (TEM) Analysis of Ni30/ZnO catalyst*

The TEM image of Ni30/ZnO catalyst showed carbon nanorods with approximate diameter of the nanorods are 5-10nm and length is found to be around 0.4µm which is shown in Fig.5.

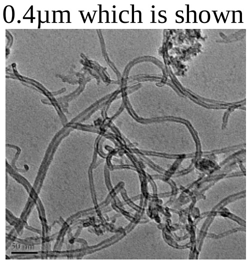

Fig.5 TEM image of Ni30/ZnO catalyst

IV. CONCLUSIONS

From the study, it can be concluded that Ni/ZnO catalyst showed optimum hydrogen production as 34.54 volume% in 60min of reaction time and then further it was decreased to 10.15 Volume% in 300min of reaction time and then catalyst deactivated at 360min. The catalyst activity decreased with the time, which points to a loss of activity due to blockage of the active sites by the carbon deposits produced during the reaction. Apart from hydrogen production, carbon nanorods were observed with a diameter and length of 5-10nm and 0.4µm for Ni/ZnO catalysts.

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