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Thermo catalytic decomposition of methane over Pd/AC and Pd/CB catalysts for hydrogen production and carbon nanofibers formation

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ABSTRACT
Hydrogen production studies have been carried using Thermo Catalytic Decomposition (TCD) Unit. Thermo catalytic decomposition of methane is an attractive route for CO_x free production of hydrogen required in fuel cells. Although metal based catalysts produce hydrogen at low temperatures, carbon formed during methane decomposition reaction rapidly deactivates the catalyst. The present work compares the results of 10 wt% Pd supported on commercially available activated carbon and carbon black catalysts (samples coded as Pd10/AC and Pd10/CB respectively) for methane decomposition reaction. Hydrogen has been produced by thermo catalytic decomposition of methane at 1123K and Volume Hourly Space Velocity (VHSV) of 1.62 L/h g on the activity of both the catalysts has been studied. XRD of the above catalysts revealed, moderately crystalline peaks of Pd which may be responsible for the increase in catalytic life and formation of carbon fibers. Also during life studies (850°C and 54 sccm of methane) it has been observed that the activity of carbon black is sustainable for a longer time compared to that of activated carbon.
***Keywords*:** Hydrogen, palladium chloride, activated carbon (AC), carbon black (CB), thermo catalytic decomposition.

I. Introduction

Hydrogen is the first element of the periodic table, making it the lightest element on earth. It is also the most abundant element of the planet, although not usually found in its pure form, H_2. This is due to the fact that it is so light; it rises into the atmospheres [1]. Hydrogen is expected to become an important fuel because of its environmental friendly nature. As it produces only water and no other pollutants on its usage in either fuel cells or IC engines it is known to be a clean fuel. Commercially hydrogen is produced by steam reforming of natural gas. Steam reforming being an endothermic process, requires huge amount of external heat. The external heat is supplied by the combustion of fossil fuels which produces huge amount of carbon dioxide. As per a study, steam reforming emits 0.43 mole of carbon dioxide per mole of hydrogen [2, 3]. As an alternative process, hydrogen production by the decomposition of methane being investigated worldwide [4-6]. Methane decomposition produces hydrogen and carbon as follows.

$CH_4 \rightarrow C + 2H_2$ $\Delta H^0_{298K} = 37{:}8$ kJ/mole of H_2 Eq. (A.1)

The energy requirement and carbon dioxide emissions for methane decomposition reaction (37.8kj/mole of H_2; 0.05 mole CO_2/mole of H_2) are lower than that of steam reforming process (63 kj/mole of H_2; 0.43 mole CO_2/mole of H_2). Also CO2 emissions can be completely eliminated by utilizing 16% of hydrogen produced during methane decomposition reaction [2, 7].

The Present work compares the results of 10wt% Pd supported on commercially available Activated Carbon and Carbon Black (samples coded as Pd10/AC and Pd10/CB respectively) for methane decomposition reaction. Hydrogen has been produced by thermo catalytic decomposition of methane at 1123K and Volume Hourly Space Velocity (VHSV) of 1.662 L/h g on the activity of both the catalysts has been studied.

II. Experimental Details

2.1 Materials

All the chemicals used for this work are purchased from Activated Carbon (AC) (Source: Coconut shells) and Carbon Black (CB) (Source: Petroleum base) M/s Active Carbon India Pvt Limited, India. Palladium Chloride (98wt% purity; M/s Fenar Reagents, India); concentrated HCl (37 wt. %; Make: M/s Qualigens, India) and HNO3 (70 wt. %; Make: M/s Merck India Ltd).Gases: Nitrogen and Methane (Purity: 99 vol %) from BOC India Ltd.

2.2 Catalyst preparation:

Activated Carbon (AC) (Source: Coconut shells) and Carbon Black (CB) (Source: Petroleum base) supported Pd catalysts have been prepared by

incipient wet impregnation technique, using AC and an alcohol solution containing appropriate amounts of $PdCl_2$ .The samples were dried overnight at a room temperature. Prior to activity test of catalyst, the samples were pre reduced at 300°C for 1hour in pure hydrogen at a flow rate of 30 SCCM. In a similar way Pd/CB catalysts also prepared.

2.3 Experimental set up and Procedure:

A bench scale Thermo Catalytic Decomposition Unit has been designed and fabricated indigenously. The bench scale unit is given below in figure 1.

Methane decomposition reaction has been carried out in an experimental set up (Fig.1) indigenously designed and fabricated. It has a Quartz tube fixed bed reactor of internal diameter 20 mm and length of 950 mm. The reactor can be heated up to 1000^0C by a split furnace. It is maintained at a constant temperature with the help of a K–type thermocouple and Honeywell microprocessor based controller. Cylindrical ceramic beads of size 5 mm (Φ) x 5mm (length) are filled in the reactor up to 75 mm length from the reactor bottom. A thin bed of quartz wool is created above the ceramic beads. Two grams of the carbon sample is placed on the quartz wool. Experiments are carried out at atmospheric pressure. Methane gas flow rate is measured with the help of calibrated Rota meter. The catalyst sample is heated to reaction temperature under nitrogen atmosphere. The reactor temperature is slowly raised to the required temperature under nitrogen atmosphere. Once the reaction temperature is attained, methane is cut into the system and nitrogen gas is closed. The gas samples are collected in Teddlar^{TM} bags at an interval of one hour for 4 hours. Methane decomposition products present in Teddlar^{TM} bags have been analyzed using Agilent 4890 gas chromatograph (TCD detector, nitrogen as carrier gas and Porapak Q column, Oven temperature: 120°C). AIMIL's Gas Chromatograph data station (DASTA-710) has been used in the analysis of gas chromatograph data.

2.4 Activity Test:

The Quartz reactor has been used in the thermo catalytic decomposition of methane activity studies of Pd10/AC and Pd10/CB catalysts. The reactor is filled up with cylindrical ceramic beads of size 5 mm (Φ) x 5mm (length) up to the center. All the catalyst samples have been ground to less than 100 micron size. A thin bed of quartz wool has been placed above the ceramic beads over which 2gms of sample is placed. As carbon samples have a tendency to decompose above 350°C [8], the reactor is heated gradually up to the reaction temperature 850°C under nitrogen atmosphere. On the attainment of the reaction temperature, nitrogen is slowly replaced with methane of purity 99.995 vol%. All experiments have been carried out under atmospheric pressure and selected temperature (850°C) at a constant methane flow rate of 54 sccm (Which corresponds to a VHSV of 1.62 Lit/hr.g). Prior to the start of each experiment, the Teddlar^{TM} bags have been flushed three times with nitrogen to avoid any contamination.The gas samples collected in Teddlar^{TM} bags at an interval of one hour for 4 hours have been analysed using Agilent 4890 gas chromatograph (TCD detector, nitrogen as carrier gas and Porapak Q column, Oven temperature: 120°C). AIMIL's Gas Chromatograph data station (DASTA-710) has been used in the analysis of gas chromatograph data.The concentrations of hydrogen and methane have been determined using the standard gases: hydrogen (99.99 vol%, BOC India Ltd) and methane (99.995 vol%, BOC India Ltd). In all the experiments no methane cracking products other than hydrogen and unconverted methane have been detected in the effluent gas. This is in confirmation with thermodynamic analysis reported in the literature which states that the thermo catalytic decomposition of methane produces only hydrogen and unconverted methane below 1127K and the reaction proceeds heterogeneously up to 900°C [9]. The amount of carbon produced has been calculated by weighing method.

The hydrogen production (volume %), methane conversion (mole %) and methane decomposition rate (mmole/min.g) of Pd10/AC and Pd10/CB catalysts have been reported in Table 1, 2 and 3 and in Figures 2, 3 and 4 respectively.

2.5 Catalyst Characterization:

Inductive coupled plasma analysis (ICP-OES)

The Composition of Pd in Pd10/AC and Pd10/CB catalysts has been measured experimentally using ICP-OES analyzer (Thermofisher Serial No: 12658, Model No. 14463001). Table 4 gives the comparison of theoretically calculated and experimentally determined Pd wt% in Pd10/AC and Pd10/CB catalysts.

BET Surface area

The N_2 BET surface area measurement has been carried out before and after catalytic test using surface area analyzer SMART SORB 93 by pre-treating the samples at 473K for 2h under nitrogen purging .Nitrogen adsorption/desorption isotherms obtained at 77K have been used to calculate BET surface area. Total pore volume (PV) has been estimated according to the Barret-Joyner-Halenda (BJH) method from the adsorption data [10].Average particle diameter is calculated using the following method [11, 12]:

Average particle diameter (Dp) = 6/ (□ p X BET SA)

Where, pp is particle density and BET SA is the BET surface area.
BET Surface area of Pd10/AC and Pd10/CB before and after reaction have been given in Table 5.

XRD Analysis

The Pd10/AC and Pd10/CB catalyst samples have been subjected to X-Ray Diffraction studies (XRD Model: Bruker d8 Advance, Germany) using CuKα as radiation source (40 kv, step size 0.02°, scan rate 0.5° $min^{1,}$ Scan angle (2θ) range of 20° ≤ 80°) have been analyzed using the Pdf-2 release ICDD data base. Coherent scattering areas have been determined by the Scherer equation [13] based on full width at half maximum of diffraction lines of {111}, {200}, {220} for Pd after test. The presence of amorphous, crystalline phases and orientation of atoms have been assessed using the database. The Fig. 5 and Fig. 6 referred for XRD micrographs of Pd10/AC and Pd10/CB samples after test.

SEM Analysis

The Surface morphology of Pd10/AC and Pd10/CB catalysts after the catalytic activity has been analyzed using Hitachi S-3700 variable vacuum SEM at an accession voltage of 15.0 KV, using a carbon conducting tape adhered on aluminum stub. The Fig. 7 and 8 referred for the SEM plots of Pd10/AC and Pd10/CB samples before and after activity tests.

III. Results and discussions

From the above Figures 2, 3 and 4 it is observed that in (i) Catalyst Pd10/AC - the percentage of hydrogen production was shown as 50.00 volume % in 1st hour and was gradually decreased to 47.00, 48.00 volume% in 2nd & 3rd hour respectively. The methane conversion was shown as 36.00 mole% in 1st hr, 31.00 mole% in 2nd hr, there was a sudden increase in the percentage at 3rd and 4th hr from 37.50 mole% to 52.50 mole%. The methane decomposition rate was shown as 0.40 mmole/min.g in 1st hr, 0.36 mmole/min.g in 2nd hr and gradually increases from 0.37 mmole/min.g to 0.65 mmole/min.g in 3rd & 4th hr.
(ii) Catalyst Pd10/CB - the percentage of hydrogen production as 38.00 volume% in 1st hr, 37.50 volume% in 2nd hr, 43.00 volume% in 3rd hr and 42.00 volume% in 4th hr. The methane conversion was shown as 25.50 mole% in 1st hr, 22.50 mole% in 2nd hr there was a sudden increase in the percentage at 3rd and 4th hr from 27.50 to 28.50 mole%. The methane decomposition rate was shown as 0.30mmole/min.g in 1st hr, 0.29 mmole/min.g in 2nd hr, 0.35mmole/min.g in 3rd hr and 0.34 mmole/min.g in 4th hr.
These trends may be explained as follows: During the activity test, BET surface area of Pd10/AC catalyst falls from 1085.05 m^2/g to 577.63 m^2/g and for Pd10/CB catalyst falls from 100.05 m^2/g to 65.17 m^2/g. Pd10/CB is lower compared to Pd10/AC. This is because CB is made up of graphite sheets, and the majority of CB is closed and blocked, due to this N_2 couldn't penetrate into the pores of CB and results lower surface area. BET Surface area of Pd10/AC and Pd10/CB before and after reaction have been given in Table 5.

The Pd10/AC is analyzed by XRD and are shown in figure 5. The presence of crystalline Pd corresponds to a very broad and high intensity diffraction peaks of {111}, {200}, {220} plane for Pd10/AC at 2θ values of (40.13°, 46.6°, 68.12°) can be observed. This XRD peak represents the typical crystalline Pd face-centered cubic (fcc) structure. It can also be observed that the shift of diffraction angles between 39.9° to 40.38° shows a lattice contraction, which implies some interaction between Pd and activated carbon. The particle size parameters are calculated from XRD spectrum data for Pd (220) reflections and its width at half peak height, the Scherrer equation have been used to calculate the average crystalline particle size of the catalyst. Pd10/AC (0.41 nm)

The Pd10/CB is analyzed by XRD and are shown in figure 6. The presence of crystalline Pd corresponds to a very broad and high intensity diffraction peaks of {111}, {200}, {220} plane for Pd10/CB at 2θ values of (39.86°, 44.09°, 64.45°), can be observed. This XRD peak represents the typical crystalline Pd face-centered cubic (fcc) structure. It can also be observed that the shift of diffraction angles between 39.86° to 40.06° shows a lattice contraction, which implies some interaction between Pd and carbon black. The particle size parameters are calculated from XRD spectrum data for Pd (220) reflections and its width at half peak height, the Scherrer equation have been used to calculate the average crystal particle size of the catalyst. Pd10/CB (0.30 nm)

The SEM analysis of both Pd10/AC and Pd10/CB catalysts is done. The morphology of the Pd10/AC in figure 7, represents the presence of crystalline Pd particles deposited on the surface of AC. The crystalline Pd particles have been evenly distributed on the surface of the AC. The average particle sizes are in range of 760 nm for Pd and 5–15 μm for activated carbon.The morphology of Pd10/CB in figure 8, shows the presence of crystalline Pd particles deposited on the surface of mesoporous carbon black. The average particle size of Pd is in range of 200 nm.

IV. Conclusions

From the above study, it is observed that both the Pd10/AC and Pd10/CB catalysts showed higher activity towards methane decomposition reaction.

The performance of Pd10/CB has been found to be the best among them because of its sustainability. During methane decomposition, Pd10 catalysts produces carbon nanofibers in the range of 200-700nm.

Pd10 catalyst has maintained its life for 4h however long duration studies may be required to assess its sustainability in the future.

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Figures:

Figure 1- Thermo Catalytic Decomposition Bench Scale Unit

Fig. 2 - Hydrogen Production (Volume %) in Pd10/AC and Pd10/CB

Fig. 3 - Methane Conversion (mole %) in Pd10/AC and Pd10/CB

Fig. 4 - Methane decomposition rate (mmole/min.g) in Pd10/AC and Pd10/CB

Fig. 5 - XRD Analysis of Pd10/AC

Fig. 6 - XRD analysis of Pd10/CB

Fig. 7 - SEM Analysis of Pd10/AC catalyst

Fig. 8 - SEM Analysis of Pd10/CB catalyst

Tables:

Table 1 - Hydrogen Production (Volume %) in Pd10/AC and Pd10/CB

Table 2 - Methane Conversion (mole %) in Pd10/AC and Pd10/CB

Table 3 - Methane decomposition rate (mmole/min.g) in Pd10/AC and Pd10/CB

Table 4 - Composition of Pd in Pd10/AC and Pd10/CB

Table 5 - BET surface area of Pd10/AC and Pd10/CB before and after reaction.

Figures:

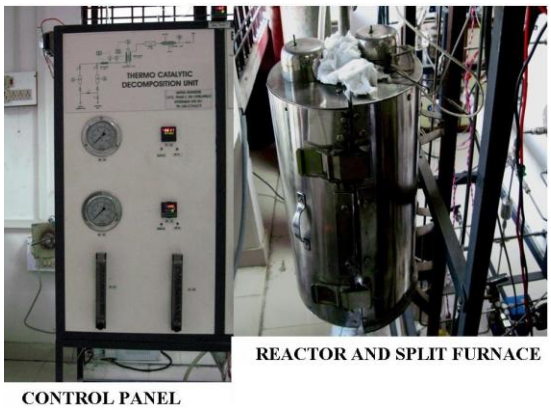


Fig. 1 - Thermo catalytic decomposition reactor setup

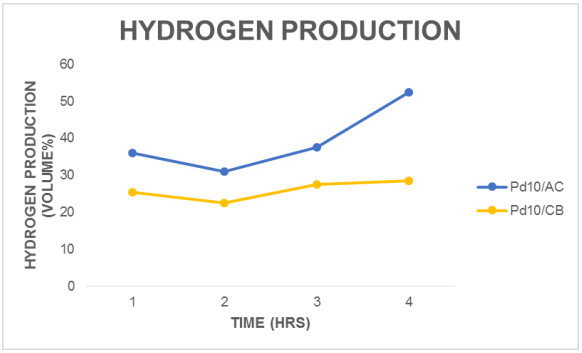


Fig. 2 - Hydrogen production (Volume %) in Pd10/AC and Pd10/CB

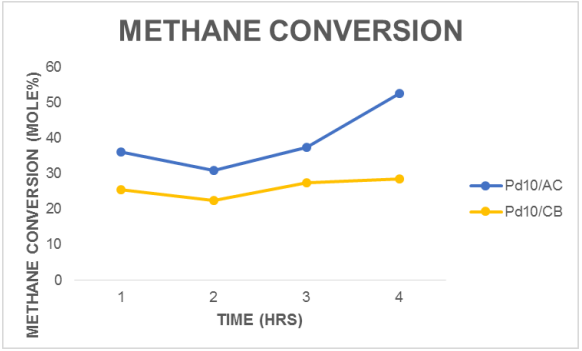


Fig. 3 - Methane conversion (mole %) in Pd10/AC and Pd10/CB

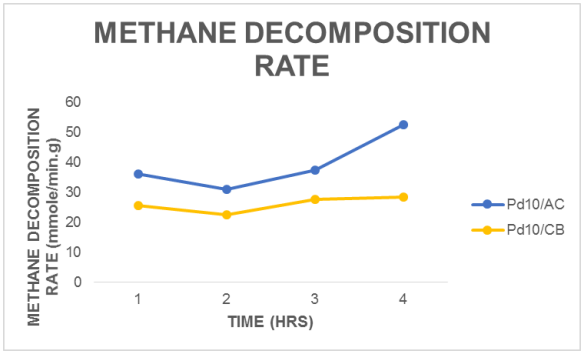


Fig. 4 - Methane decomposition rate (mmole/min.g) in Pd10/AC and Pd10/CB

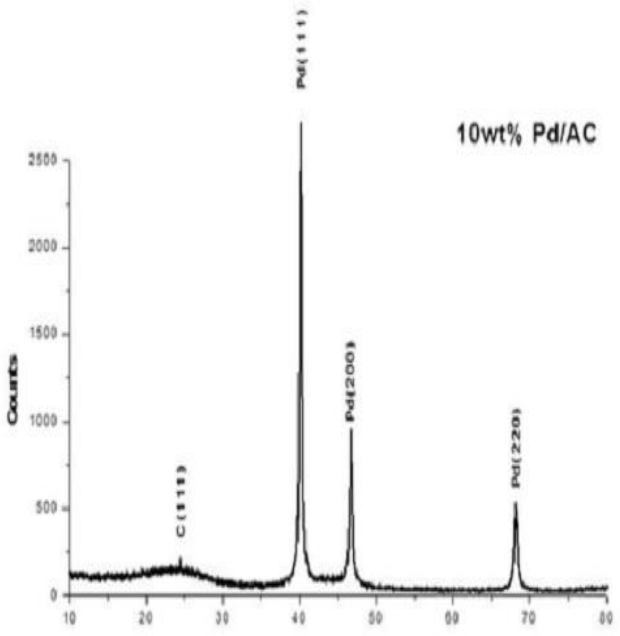


Fig. 5 - XRD Analysis of Pd10/AC

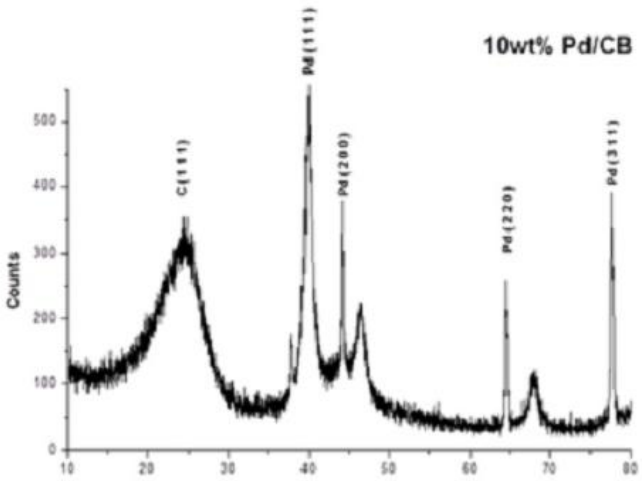
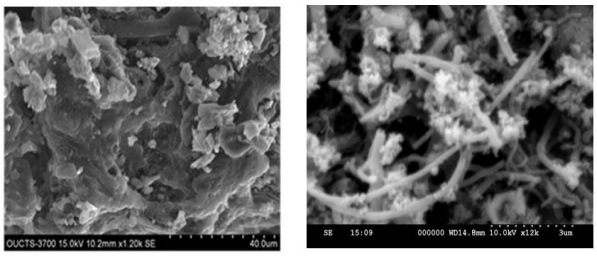
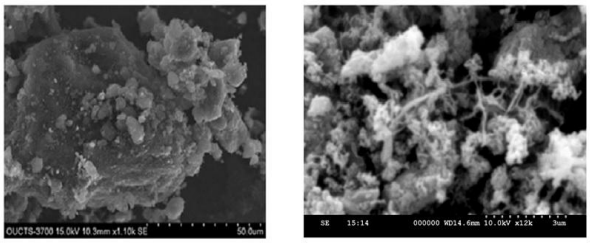


Fig. 6 - XRD analysis of Pd10/CB



Pd10/AC catalyst before test Pd10/AC catalyst after test

Fig. 7 - SEM Analysis of Pd10/AC catalyst



Pd10/CB catalyst before test Pd10/CB catalyst after test

Fig. 8 - SEM Analysis of Pd10/CB catalyst

Tables:

Table 1 - Hydrogen production (Volume %) in Pd10/AC and Pd10/CB

Time (Hrs)	Hydrogen Production (Volume %)	
	Pd10/AC	Pd10/CB
1	50	38
2	47	37.5
3	48	43
4	72	42

Table 2 - Methane conversion (mole %) in Pd10/AC and Pd10/CB

Time (Hrs)	Methane Conversion (mole %)	
	Pd10/AC	Pd10/CB
1	36	25.5
2	31	22.5
3	37.5	27.5
4	52.5	28.5

Table 3 - Methane decomposition rate (mmole/min.g) in Pd10/AC and Pd10/CB

Time (Hrs)	Methane Decomposition Rate (mmole/min.g)	
	Pd10/AC	Pd10/CB
1	0.4	0.3
2	0.36	0.29
3	0.37	0.35
4	0.65	0.34

Table 4 - Composition of Pd in Pd10/AC and Pd10/CB

Sample Code	Wt% of Pd (Calculated)	Wt% of Pd (ICP-OES), JNTU-Hyderabad
Pd10/AC	10	8.5
Pd10/CB	10	8.6

Table 5 - BET surface area of Pd10/AC and Pd10/CB before and after reaction.

Sample Code	BET SA before test (m^2/g)	BET SA after test (m^2/g)	Percentage loss in area (%)
Pd10/AC	1085.05	577.63	62
Pd10/CB	100.05	65.17	65