

Catalytical Effect of Fluka 05120 on Methane Decomposition

Vidyasagar Shilapuram, Nesrin Ozalp, and Anam Waheed

Abstract—Carboneous catalytical methane decomposition is an attractive process because it produces two valuable products: hydrogen and carbon. Furthermore, this reaction does not emit any green house or hazardous gases. In the present study, experiments were conducted in a thermo gravimetric analyzer using Fluka 05120 as carboneous catalyst to analyze its effectiveness in methane decomposition. Various temperatures and methane partial pressures were chosen and carbon mass gain was observed as a function of time. Results are presented in terms of carbon formation rate, hydrogen production and catalytical activity. It is observed that there is linearity in carbon deposition amount by time at lower reaction temperature (780 °C). On the other hand, it is observed that carbon and hydrogen formation rates are increased with increasing temperature. Finally, we observed that the carbon formation rate is highest at 950 °C within the range of temperatures studied.

Keywords—Catalysis, Fluka 05120, Hydrogen production, Methane decomposition

I. INTRODUCTION

HYDROGEN production via methane decomposition is highly favorable because of the carbon byproduct with no emissions. Non-catalytical decomposition of methane requires high temperatures at above 1000°C for the reaction to reach equilibrium [1], thus a catalyst is preferred. Catalysts of carbonaceous samples over methane decomposition have been previously studied by others [2-7], and by our research group [8, 9]. Alternatively, transition metal catalysts have been also studied by various groups and it was concluded that catalyst deactivation through carbon deposition in the active sites and carbon-metal separation were the major problems in using them [10]. Carbon catalysts offer many advantages over transition metal catalysts such as lower costs, temperature resistance and no need for separation of catalyst from the products [1]. As for the carbon laden flows in a solar reactor, carbon particle addition as a catalysts has a good impact on methane to hydrogen conversion because of enhancing the heat transfer by absorbing radiation, and serving as nucleation sites. One of the earlier studies stated that the characteristics of

carbon sample has significant effect on the catalytic activity and therefore ultimately affects the methane decomposition rate [11]. Some of these factors include crystallographic structure, surface area and surface groups of the carbon samples as discussed in [9]. Consequent studies performed on comparing characteristics of carbon blacks with commercial activated carbon showed that the total pore volume of the fresh catalysts has a linear relationship with the amount of carbon deposited until deactivation [4]. Another correlation in this study was found between the initial reaction rate and the concentration of oxygenated groups desorbed as CO after a temperature-programmed desorption (TPD) experiment.

Recently, researchers have used thermogravimetric analyses (TGA) to study methane decomposition with different catalysts such as carbon blacks, activated carbons and ordered mesoporous structure carbons [3-5] and [12]. However, during methane decomposition with carbon catalyst, carbon samples are also subject to deactivation and it was determined that activated carbons with micro and mesoporosity deactivate faster than ordered mesoporous structures. Botas et al. [5] found that the CMK-5 is a more favorable catalyst for the decomposition than the carbon blacks or the activated carbons. Since the activated carbons deactivated the fastest, carbon blacks are thus the more favorable commercially available carbon catalysts. Pinilla et al. [3] compared carbon black (BP2000) and activated carbon (CG Norit) in a kinetic study for use as catalysts in the thermo-catalytic methane decomposition reaction. TG analysis demonstrated that activated carbon becomes rapidly deactivated after high initial activity while the carbon black activity is lower and has a 600% mass increase so is one order of magnitude higher than that of activated carbon [3].

Previously, we presented the comparison of two activated charcoal samples, Fluka 05105 and Fluka 05120, to compare their catalytical characterization with TG analysis [9]. As a follow up study, we presented in-depth TG analysis of the methane decomposition reaction using the same two carbon samples as catalysts [10]. We found that the threshold temperature of Fluka 05120 is higher than that of Fluka 05105. With the same experimental conditions, Fluka 05105 demonstrated maximum hydrogen production and carbon formation, thus showing better catalytic activity than Fluka 05120. In this paper, we expand our experimental run conditions by performing tests at different methane volume percentages and temperatures. We present the results of carbon weight gain as the progress of reaction, carbon formation rate, hydrogen production, and the catalytical activity of this particular carbon as a catalyst.

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II. EXPERIMENTAL METHODOLOGY

We have used Fluka 05120 as the catalyst, methane as the auxiliary gas, and helium as the carrier gas in our thermogravimetric analyser (TGA) by Setaram (Setsys evolution 16/18, M/s). We have recorded carbon mass change and observed carbon deposition in the crucible. The crucible used in these experiments is made of PtRh 10% and has 130 μL volume. We have tested various temperature and partial pressures of methane, where the summary of the run conditions are given in Table 1. The maximum auxiliary gas (methane) volume percentage was 50% because of the limitations of the thermogravimetric analyzer. With the Setsys evolution 16/18, the carrier gas flow rate can be varied from 4 to 200 ml/min, and the auxiliary gas flow can range between 0.3 and 16 mL/min. These minimum and maximum values were originally set for air. Therefore, in order to determine the minimum and maximum values flow rates for other gases, a correction coefficient needs to be calculated, and used to recalculate the flow rates. We calculated that the correction factor for He is 1.4 and for methane it is 0.72. Accordingly, we can vary the carrier gas flow rate from 5.6 to 280 ml/min, and the methane gas flow rate from 0.21 to 11.5 ml/min.

Once the weighed sample is put in the crucible of the TGA's furnace, a high flow rate of helium gas is used to purge the reaction chamber and to fill up the furnace after a vacuum was created. In order to remove air and moisture, a maximum flow rate of 280 ml/min is used so that we prevent catalyst oxidation. Five runs were performed for the experiments with Fluka 05120 at different temperatures and methane volume percents, as shown in Table 1.

TABLE I
EXPERIMENTAL RUN CONDITIONS FOR TESTING FLUKA 05120

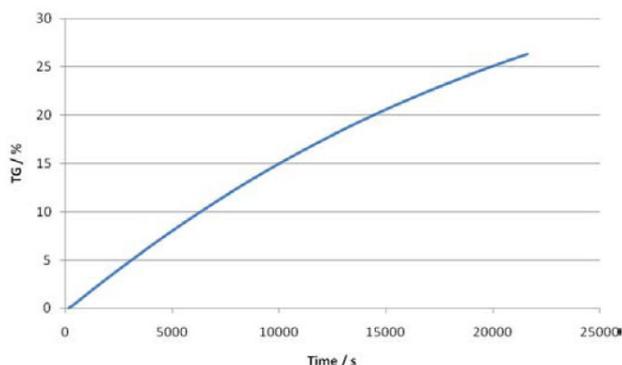
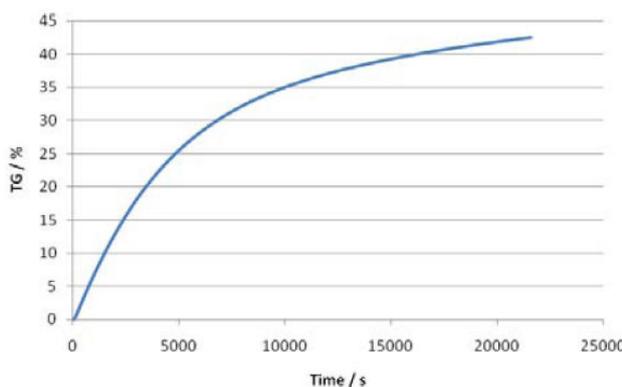
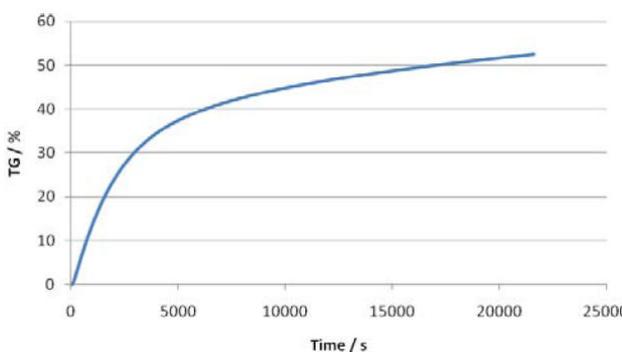
Run	Temperature, °C	Actual flow rates, ml/min			CH ₄ Vol %
		Auxiliary (CH ₄)	Carrier (He)	Total flow	
1	950	10	30	40	25
2	900	10	30	40	25
3	850	10	30	40	25
4	780	10	10	20	50
5	880	10	10	20	50

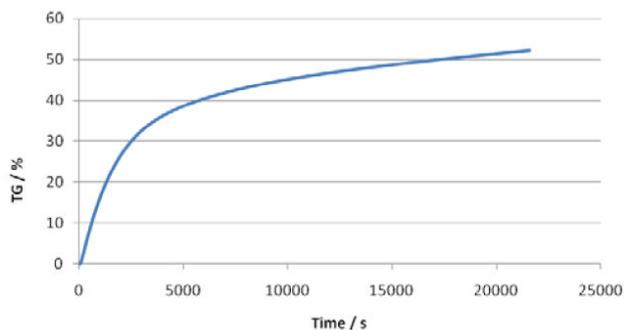
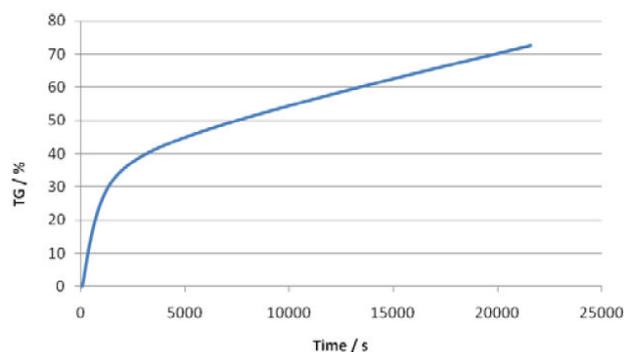
III. RESULTS AND DISCUSSION

Different temperatures and methane volume percentages are chosen such that they are different from our previous work in [8] and [9] so that we obtain more comprehensive analysis. We used one template of the temperature program for all 5 experimental runs beginning from 40 °C and a ramp rate of 30 °C per minute, to reach the desired temperature with the inert carrier gas (He). Once the desired temperature is reached then methane gas is introduced along with the carrier gas (this is called reaction zone). The reaction zone lasts approximately 6 hours for each experimental run. As mentioned previously, flow rates are chosen such that the desired volume percentage of methane is maintained in the feeding gas. After completion of reaction zone, auxiliary gas (CH₄) is shutoff by only running the helium gas at maximum possible flow rate (280 ml/min)

with a ramp rate of 99 °C per minute until the furnace is brought down to 20 °C.

The results of these experiments are shown in Fig. 1 for activated charcoal sample, Fluka 05120. It is evident that carbon mass gain is very similar order of magnitude for all experiments and that the reaction does occur at 780 °C but at much faster rate at higher temperatures.

Fig. 1a CH₄ decomposition at 780 °CFig. 1b CH₄ decomposition at 850 °CFig. 1c CH₄ decomposition at 880 °C

Fig. 1d CH₄ decomposition at 900 °CFig. 1e CH₄ decomposition at 950 °C

Carbon mass gain is defined as the weight of carbon deposition (C_{dep}) per initial weight of Fluka 05120 catalyst (C_{cat}) taken. The effect of reaction temperature and volume percent of methane on carbon mass gain is shown in Fig. 2. The two figures for carbon mass gains are plotted versus time at methane volume percentages of 25% (Fig. 2a) and 50% (Fig. 2b).

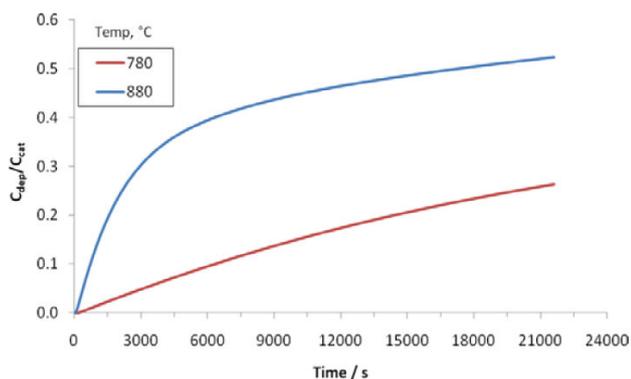


Fig. 2a Carbon mass gain at 50 vol.% methane

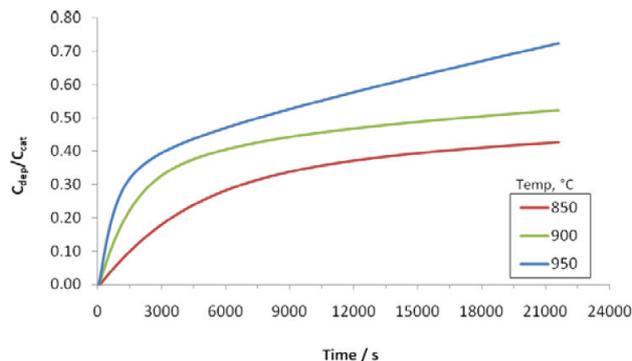


Fig. 2b Carbon mass gain at 25 vol. % methane

Initial increase in mass over Fluka 05120 is seen with increasing temperature. It is evident that the mass gain at higher temperatures (850, 900 and 950 °C) is much more rapid than that at lower temperatures (780 and 880 °C). Ultimate mass gain is defined as the maximum weight of the carbon deposited per gram of initial catalyst sample taken. As shown in fig. 2, ultimate mass gain depends on temperature and shows that the ultimate mass gain is 0.72, 0.52 and 0.43 g C / g cat for reaction temperatures of 950, 900 and 850 °C, respectively. Our ultimate mass gain at 900 °C corroborates the findings of Suelves et al. [4] closely, who reported a finding of 0.49 which gives a percent error of 6.1%.

Carbon formation and hydrogen production increase with increasing methane volume percent. If we refer to Pinilla et al. [3], they claim that the ultimate ratio of deposited carbon to initial carbon catalyst weight is independent of temperature. In our study, we observed the opposite. This could be because of the different run conditions we used in our experiments as well as the difference in carbon catalyst sample, which were CG Norit and BP 2000 samples in their case. Our results have been supported with the results of Abbas and Daud [12] to some extent. They demonstrated that different ultimate mass gains resulted for different temperatures of activated carbon from palm shell based carbon samples.

For different temperatures, the change of molar formation rate of carbon with time is presented in Fig. 3. The reaction at 950 °C has the highest carbon molar formation rate of 1.94 mmol/g_{cat} min, whereas that for 850 °C has a maximum rate of 0.38 mmol/g_{cat} min. Almost exponential decay is observed after the carbon sample reaches its maximum value. At lower temperatures of 900 and 850 °C, the formation rate is smaller but takes longer time to become insignificant.

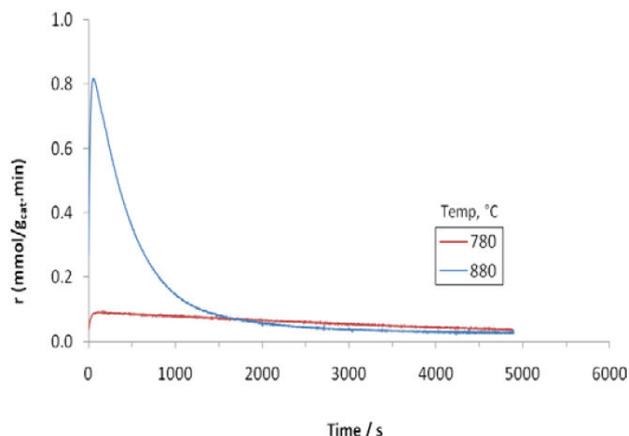


Fig. 3a Rate of carbon formation vs. time for different temperatures at methane volume percent 50%

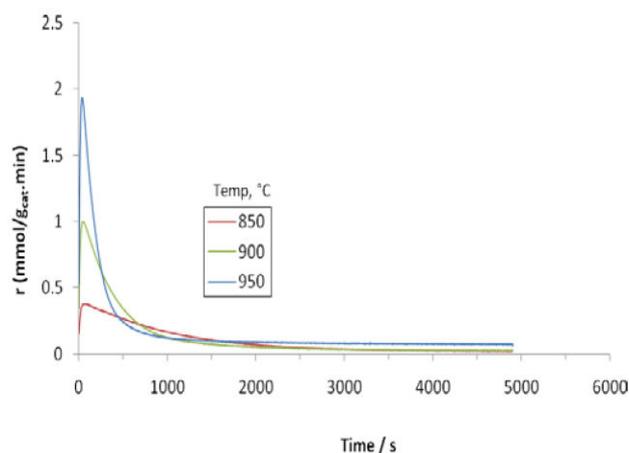


Fig. 3b Rate of carbon formation vs time for different temperatures at methane volume percent 25%

For different methane partial pressures, the change in activity with time is shown in Fig. 4. Activity is calculated from:

$$a(t) = \frac{r_c(t)}{r_0} = 1 - \frac{C(t)_{dep}}{C_{CM}} \quad (1)$$

where;

$r_c(t)$ – rate of carbon formation at time ‘t’

r_0 – initial rate of carbon formation

$C(t)_{dep}$ – weight of carbon deposited at time ‘t’

C_{CM} – maximum weight of carbon deposited

Comparison of the activities for Fluka 05120 shows that the decay in its activity is higher at elevated temperatures, highest at 950 °C. At lower temperature of 780 °C activity is decreasing linearly with time at 50 vol. % methane partial pressure as shown in Fig. 4b. Whereas activity variation with time noticed is different for rest of the temperatures for different methane vol. % as shown in Fig 4a and Fig. 4b.

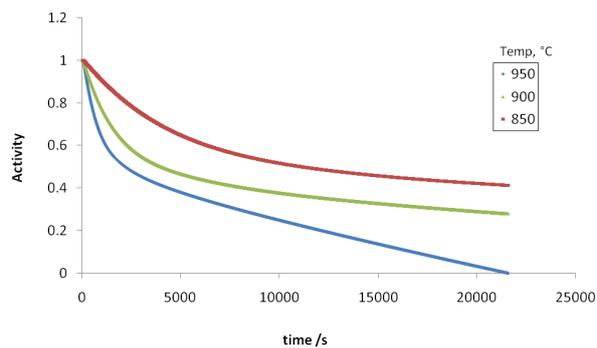


Fig. 4a Activity at 25 vol. % methane for different temperatures

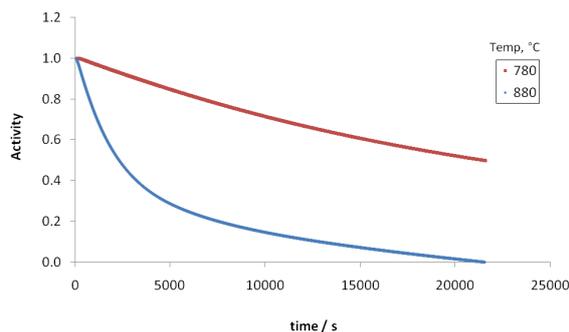


Fig. 4b Activity at 25 vol. % methane for different temperatures

Table II demonstrates a general increase in the hydrogen and carbon production rate over the course of the methane decomposition reaction with Fluka 05120 as catalyst. However, close examination of both rates at 880 and 900 °C shows a decrease. This can be attributed to the greater effect of the methane volume percent or because of difference in total flow rate on the reaction.

Ultimate carbon weight gain was calculated using the TG (mg) value of the pure carbon formed in the crucible of the reaction furnace. This value was divided by the total mass of initial catalyst sample used to give a rate in $\text{mg}_{\text{carbon}} \text{mg}^{-1}_{\text{catalyst}}$. Average hydrogen production is calculated using the stoichiometric molar ratio of carbon to hydrogen in the overall equation:

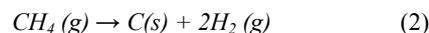


TABLE II
AVERAGE HYDROGEN AND CARBON PRODUCTION RATES WITH FLUKA 05120 AS CATALYST IN METHANE DECOMPOSITION REACTION

Temperature (°C)	CH ₄ vol. %	H ₂ (mmolmin ⁻¹ g ⁻¹)	Ultimate carbon weight gain (mg _{carbon} .mg ⁻¹ _{catalyst})
780	50	0.1217	0.2635
880	50	0.2420	0.5244
850	25	0.1964	0.4260
900	25	0.2415	0.5220
950	25	0.3351	0.7244

Thus, according to Table II, Fluka 05120 exhibits better catalytic activity at higher temperatures with higher methane partial pressures.

IV. CONCLUSION

We presented experimental results of our thermogravimetric analysis using Fluka 05120 as the catalyst to study its effect on methane decomposition. Experiments were performed at different temperatures and methane volume percent in the feed gas to determine the effects of each on the reaction. For reactions occurring at 50 vol. % methane, lower temperatures, e.g. 780 °C, showed greater linearity in illustrating the relationship between the carbon deposition amount over the total mass of carbon used. This proportionality is not seen for reactions occurring at 25 vol% methane. It is also evident that at a fixed methane volume percent, the rate of carbon deposition per mass of catalyst gets higher with increasing temperatures. Therefore, we observed that the rate of carbon formation is highest at 950 °C. It was found out that the ultimate carbon mass gains are directly proportional to the reaction temperature and the maximum ultimate mass gain was observed at 950 °C with 0.72 g_c/g_{cat}. The decay in activity was found to be highest for the reaction at 950 °C. Finally, we observed that the carbon and hydrogen formation rates increase with increasing temperature.

ACKNOWLEDGEMENT

This research has been funded by National Priorities Program of Qatar National Research Fund (QNRF) Project No: NPRP 09-671-2-255. Support for the undergraduate students working on this project has been funded by QNRF Undergraduate Research Experience Program Project No: UREP 10-122-2-037.

NOMENCLATURE

$a(t)$	Catalyst activity
C_{dep}	Amount of carbon deposited, mg
C_{cat}	Initial carbon catalyst weight, mg
r	Carbon formation rate, mmol/g _{cat} .min
TG	Percentage carbon mass gain, %

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