

## COMPARISON OF CATALYST ACTIVITY BETWEEN PALLADIUM, COPPER AND IRON CATALYST IN CATALYTIC COMBUSTION OF METHANE

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### ABSTRACT

Catalyst used for high-temperature combustion of light hydrocarbon for example methane must maintain high activity over long time intervals by avoiding excessive sintering and deactivation in the hot and corrosive combustion environment. This study is carried out to compare the catalyst activity between Palladium, Iron and Copper catalyst in the catalytic combustion of methane. The characteristics of catalyst are studied with NA and SEM. In this characterization method, the catalyst morphology and the surface areas of the catalyst can study. This research is carried out in the micro reactor in laboratory scale. The effect of Hydrogen Sulphide, H<sub>2</sub>S poisoning on the combustion of methane over alumina-supported also investigates. From the result obtain, Pd/Al<sub>2</sub>O<sub>3</sub> is the most active catalyst and stable follow by Cu/Al<sub>2</sub>O<sub>3</sub> and Fe/Al<sub>2</sub>O<sub>3</sub>. BET characterization shows that, all catalyst loss its specific surface area when poison with H<sub>2</sub>S and increase follow the order Pd > Cu > Fe.

**Key Words:** Methane-combustion, Catalyst activity, Sulphur, Deactivation, Regeneration

### 1.0 INTRODUCTION

Nowadays natural gas is widely used in many sectors. This is because natural gas is an abundant and relatively clean fuel with large reserve. Catalytic combustion offers an alternative means of producing energy. A wide range of concentrations of hydrocarbon can be oxidizing over a suitable catalyst, and it become possible to work outside flammability limits of fuel [1]. The use of catalysts such as platinum and palladium leads to a decrease of pollutant emissions in gas burners and turbines [2 - 4]. For instance, the catalyst allows running of the combustion process at a lower temperature resulting in lower thermal NO<sub>x</sub> formation. The reactions condition can control more precisely and the reaction temperature can maintain below 1600°C [1]. Besides that, the catalytic combustion can reduce producing of carbon monoxide CO, sulphur oxides SO<sub>x</sub> and unburned hydrocarbons by only produce carbon dioxide and water vapor.

In contrast with conventional combustion, catalytic combustion does not requires the presence of a flame, nor an ignition source like a spark or pilot flame, nor is it bound by flammability limits, nor is it penalized by severity of the conditions within a flame. There is a minimum inlet gas temperature required to have a sufficiently high catalyst activity to achieve complete combustion. As we know, the efficiency of methane combustion can be enormously increased by carrying out the reaction in the presence of a catalyst. The group VIII metals of periodic table are found to active catalysts catalytic combustion. Noble metals are the most suitable and sufficiently active. Some of them are too expensive for general commercial use. Others metals such as Cr, Mn, Fe, Cu and Ni show good potential as combustion catalysts. With a suitable catalyst choice, the activation energy for heterogeneous

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catalytic reaction is much lower than that of the purely homogeneous flame reaction. During the use of the catalyst in the combustion process, the catalyst activity gradually declines. This is due to the deactivation or degradation resulting in a change of physical and chemical nature. Consequently, heterogeneous oxidation rates can be achieved for temperatures and fuel concentrations much lower than those required for the homogeneous reaction.

The catalytic oxidation is dependent on some factors such as oxygen : methane feed ratio, the loading of precious metal on the support, the nature of the support, the particle size of precious metal and the extent and nature of catalyst pretreatment [1]. Meanwhile the reaction rate is dependent on methane concentration and the oxygen pressure is depending on operating conditions. The catalyst system is in general composed of two components, which are the support system and the active material. The functions of support system are to increase the surface area of the metal or the metal oxide by providing a matrix that enables their dispersion as very small particles, reduces sintering of the active catalyst material and enhances the activity of the catalyst. Active material (catalyst) is function to initiate the catalytic oxidation of fuel at the lowest reaction temperature and possess high catalytic activity.

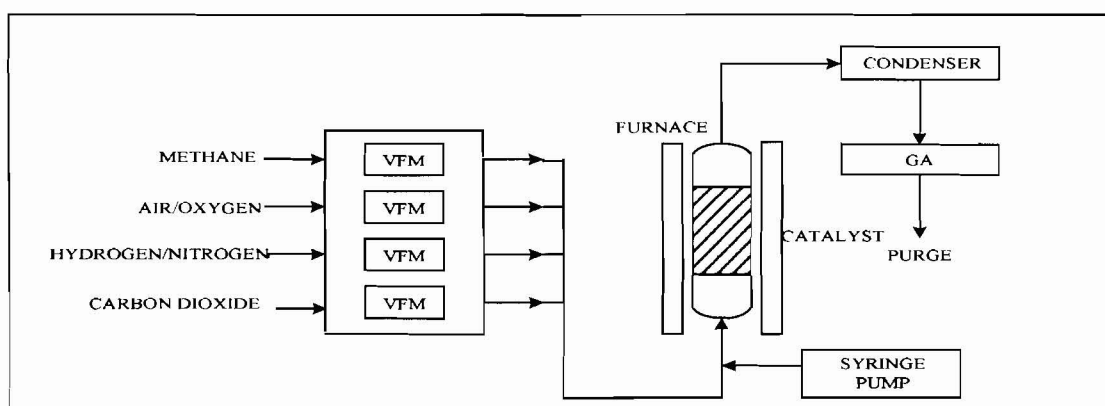
In the catalytic combustion application, the small amounts of sulphur compounds are present in the feed gas [5]. The existing of sulphur may react to produce sulphur dioxide, sulphur trioxide and sulphate species. When the sulphate groups adsorbed on Pd particles, it deactivates the catalytic activity.

## **2.0 MATERIALS AND METHODS**

### **2.1 Catalytic Measurement**

The catalytic activities of Pd/Al<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> for methane combustion were measured using a micro reactor. The catalyst sample will be placed onto the quartz sinter layer inside the middle of the reactor. The reactor will be situated in the centre of heating element of an electrical furnace in order to get the thermal energy supply. The feed gas will flow upward inside the reactor and pass through the catalyst where the reaction takes place, and the combustion products purge out to atmosphere through a tube line that will be connected to the top part of reactor. A thermocouple attached to the external side of the reactor wall was used to measure the reaction temperature. Total flow rate of feed was 100 mL/min with 4 vol. % of pure methane gas; the balance is oxygen and nitrogen gases. The methane conversions are measured at each temperature range until it achieves 100% conversion. This combustion product will be analyzed by gas analyzer. For catalytic combustion of methane in the poisoned catalyst, 10 ppm H<sub>2</sub>S is injected into the rig and flows continuously with feed flow. Regeneration of poisoning catalyst was done with regenerate the catalyst with H<sub>2</sub>. Figure 1 shows the set up of the catalyst activity experimental test rig.

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**Figure 1** Schematic Diagram of Experimental Rig for Catalyst Activation

### 2.2 Catalyst Characterization

The Scanning Electron Microscope (SEM) characterization is conducted using Gemini Column to collect data about catalyst morphology such as catalyst distribution and particle size. The samples were glued to the sample holder and analyze. The BET surface area of solid was determined using a Quantachrome Nova 1000 Sorptometer. The samples were evacuated for 2 hour before measuring the surface area. The surface areas were measured by Nitrogen Adsorption at 77K.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Catalytic Combustion of Methane

This study is done to compare the activities of catalyst used at poisoning and regeneration condition. Catalyst activity is measured based on function of time at different temperature until a steady state is obtained which means 100% methane conversion. Figures 2–3 show the fraction of methane conversion using the following catalysts: Pd/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> and Fe/Al<sub>2</sub>O<sub>3</sub> as a function of reaction temperature.

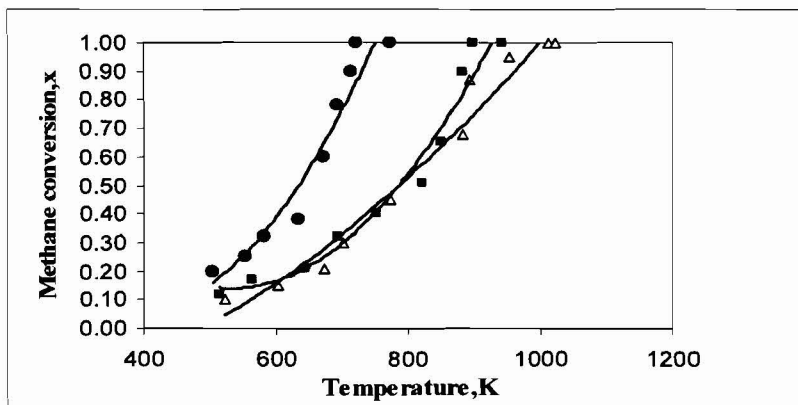
It can be observed from the graphs plotted below, that catalyst activity for poisoned catalyst and regenerate catalyst increased in the following order: Pd > Cu > Fe. When the catalyst poisoned with sulphur, all catalyst required higher temperature to achieve 50% methane conversion. After regeneration with hydrogen gas all catalysts recover some of their activity and the temperature required to achieve 50% methane conversion much lower. These are due to the chemisorption of sulphur on the active sites of the catalyst and totally or partially inhibit the adsorption or the dissociation of molecular species and inhibit the surface reaction between adsorbed species. From the data gain, Pd catalyst is the most active catalyst compare to Cu and Fe catalyst because less deactivate by sulphur and recover most of activity after regeneration beside required lower temperature to achieved 50% methane conversion.

From Arrhenius plot below, a linear relationship is obtained at 50% methane conversion. After 50% methane conversion, diffusion regime is achieved. At 50% and 100%

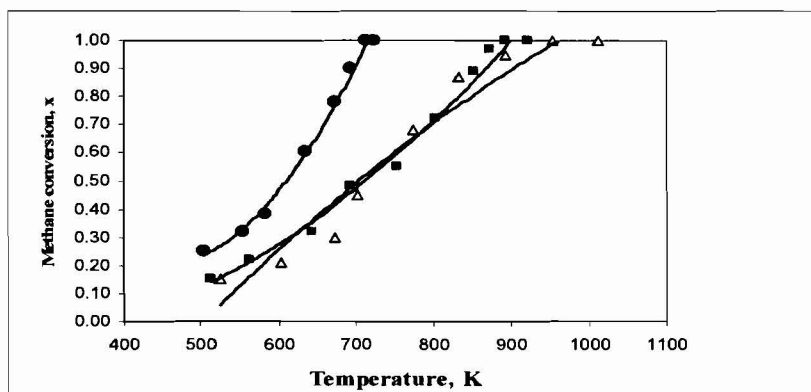
methane conversion, the corresponding temperature for each catalyst is tabulated in Table 1. Kinetic regime is achieved until a 50% maximum conversion of methane for every types of catalyst used. In kinetic regime, activation of catalyst activity and catalyst ability to increase rate of reaction are important. This is because catalyst is needed to increase rate of reaction between reactants at low temperature. The more active a catalyst is, the lower temperature is needed to achieve 50% methane conversion, and this implies the catalysts is suitable for low temperature application beside less or no NO<sub>x</sub> produce and avoid catalyst sintering.

In diffusion regime, higher temperature is needed to attain steady state. Thus, this regime is more suitable for high temperature application like gas turbine (1250-1500°C) and fluidized bed. Normally in high temperature application, non-porous catalyst is used. Although there is sulphur poisoning in catalyst which can deactivate catalyst activity, but in diffusion regime catalyst will still achieve 100% methane conversion because the catalyst is self-generated.

If the catalyst is heated excessively beyond a critical temperature, the high concentration of vapors can also lead to the transport of significant amounts of catalytic materials to either substrates where they can react, or into the gas phase where they are lost in the effluent gas stream. For noble metals such as Pd, Ir, Pt and Ru, Pd is the most superior with respect to vaporization for temperatures below 1000°C and followed by Ir, Pt and Ru.



**Figure 2** Methane conversion with temperature for poisoned catalyst  
● Pd/Al<sub>2</sub>O<sub>3</sub>, ■ Cu/Al<sub>2</sub>O<sub>3</sub> and Δ Fe/Al<sub>2</sub>O<sub>3</sub>



**Figure 3** Methane conversion with temperature for regenerate catalyst  
● Pd/Al<sub>2</sub>O<sub>3</sub>, ■ Cu/Al<sub>2</sub>O<sub>3</sub> and Δ Fe/Al<sub>2</sub>O<sub>3</sub>

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The first row transition metal oxides are also surprisingly volatile. Iron appears to possess the most stable oxide with acceptable volatility to temperatures as high as 1000°C. Copper, its volatility rises well above 100 ppm at 1000 °C[6].

### 3.2 Catalyst Activity Measurements

Mass-specific reaction rate constant,  $k_m$  is used to calculate catalyst activity rate in reaction at 623K. From data obtained, all the catalysts decrease their activities when poisoned with sulfur as shown in Figure 2. This is because the accumulation of impurities on the active sites blocks the access of reactants to these active sites. After regeneration, the activities of the catalyst increase compared to the poisoned state (as shown in Figure 3), because regenerative hydrogen gas reduces the oxidized sulphur species back to  $\text{SO}_2$  which is subsequently desorbed from the catalyst. It is found that the catalyst activity rate for  $\text{Pd}/\text{Al}_2\text{O}_3$  is higher than  $\text{Cu}/\text{Al}_2\text{O}_3$  and  $\text{Fe}/\text{Al}_2\text{O}_3$  catalysts either in the poisoned or regenerate catalyst states.

Catalyst activity increases with the increment of atomic number of metal used. The low activity of metals appearing early in the transition series is a consequence of a limited number of surface sites available for chemisorptions owing to the smaller number of d electrons. Catalytic abilities of transition metals originate in the drawing of electron from chemisorbed species into the d electron band, which weakens or destroys bonds in the original molecule.

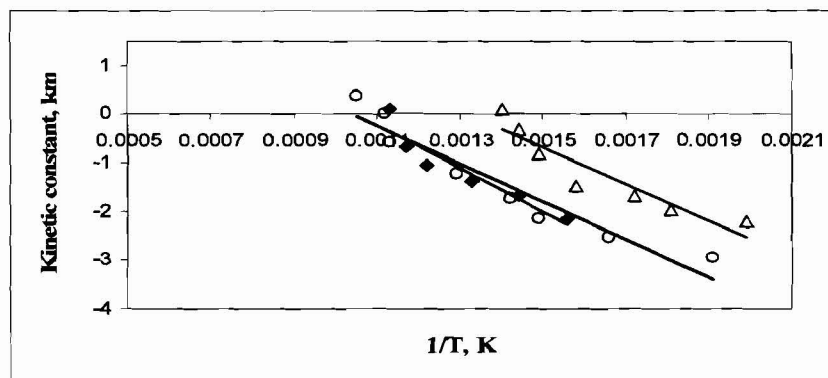


Figure 4 Kinetic constant at the temperature function for poisoned catalyst  $\Delta$   $\text{Pd}/\text{Al}_2\text{O}_3$ ,  $\blacklozenge$   $\text{Cu}/\text{Al}_2\text{O}_3$  and  $\circ$   $\text{Fe}/\text{Al}_2\text{O}_3$ .

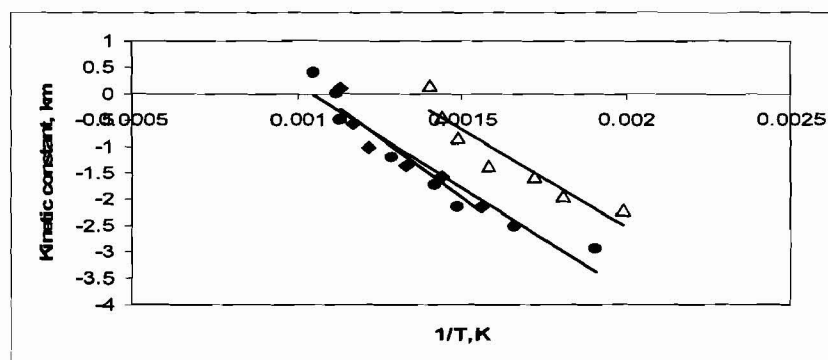


Figure 5 Kinetic constant at the temperature function for regenerate catalyst

$\Delta$  Pd/Al<sub>2</sub>O<sub>3</sub>,  $\blacklozenge$  Cu/ Al<sub>2</sub>O<sub>3</sub> and  $\circ$  Fe/ Al<sub>2</sub>O<sub>3</sub>.

Figures 4 – 5 display Arrhenius plot for catalyst samples Pd/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> and Fe/Al<sub>2</sub>O<sub>3</sub> at the poisoned and regenerated conditions, respectively.

For the activation energy,  $E_A$ , Pd catalyst required lower activation energy in mostly pretreatment condition followed by Cu and Fe catalyst. Catalyst that has been poisoned with H<sub>2</sub>S gas needs higher activation energy to start a reaction. This is due to the presence of sulphur element which deactivates most of the active sites on catalyst. Meanwhile for frequency factor, A, Pd catalyst have higher frequency factor compare to the Fe and Cu catalyst. The more higher the frequency factor, the more molecules can absorb on the surface of the catalyst. This will increase the catalyst activity.

**Table 1** Kinetics rate data's for combustion of methane over precious metals catalysts under different pretreatment conditions.

| Catalyst                          | Pretreatment conditions | $E_a$<br>(kJ/ mol) | A<br>(cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> ) | $k_{m623}$<br>(cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> ) | T <sub>50</sub><br>(K) | T <sub>100</sub><br>(K) |
|-----------------------------------|-------------------------|--------------------|---|--|------------------------|-------------------------|
| Pd/Al <sub>2</sub> O <sub>3</sub> | Poisoned                | 31.4136            | 0.1455E+03  | 2.002  | 675                    | 723                     |
|                                   | Regenerated             | 28.4322            | 0.2318E+03  | 2.425  | 610                    | 713                     |
| Cu/Al <sub>2</sub> O <sub>3</sub> | Poisoned                | 37.3955            | 0.1147E+03  | 0.973  | 817                    | 898                     |
|                                   | Regenerated             | 34.7697            | 0.45974E+03   | 1.287  | 710                    | 893                     |
| Fe/Al <sub>2</sub> O <sub>3</sub> | Poisoned                | 45.5092            | 0.3833E+03  | 0.797  | 797                    | 1013                    |
|                                   | Regenerated             | 40.3391            | 0.4635E+03  | 1.028  | 708                    | 953                     |

### 3.4 Catalyst Characterization

#### 3.4.1 Scanning Electron Microscope (SEM)

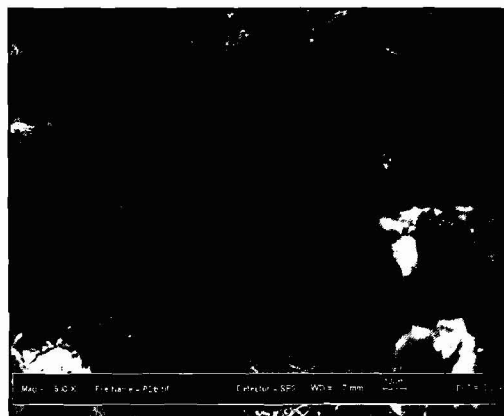
The size of the metal particles plays a crucial role for the catalyst efficiency, and the determination of size distribution is one of the main tasks of electron microscopy in catalysis. Figures 6 - 8 below show the distribution of particles and particle size of Pd, Cu and Fe catalysts in calcined condition with magnification 100X and 500X.

Particles distribute uniform in the Pd and Cu catalyst but distributes un-uniformly in the Fe catalyst like an island. If catalyst particles distribute uniform in the support, it will increase the surface area of the catalyst, but if distributes like an island, the surface area of the catalyst will decrease and indirectly this will cause less amount of surface for the reaction of reactants occurs. From the figures below, the mean diameter of particles at 500 times magnification. The mean diameter of particles for Pd/Al<sub>2</sub>O<sub>3</sub> catalyst is 0.02 mm and 0.018 mm for Cu/Al<sub>2</sub>O<sub>3</sub> and Fe/Al<sub>2</sub>O<sub>3</sub> catalyst respectively.

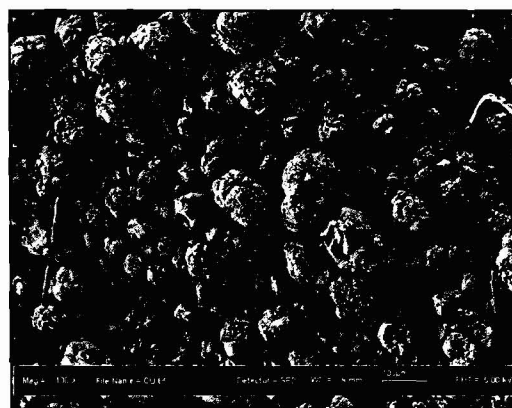
As the mean average of particles become lesser, the surface areas of the particles increase. High surface area of the catalyst will cause increasingly the numbers of surface where the reaction can occurs and indirectly will yield in high catalyst activity. However, the

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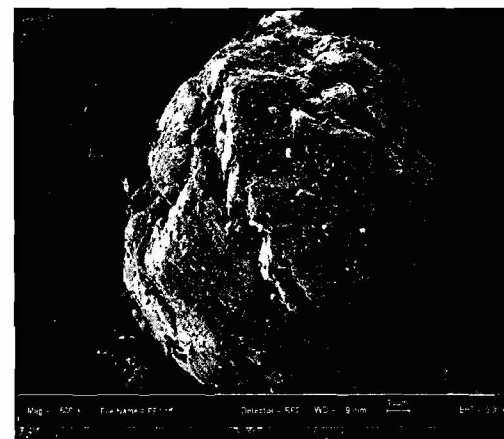
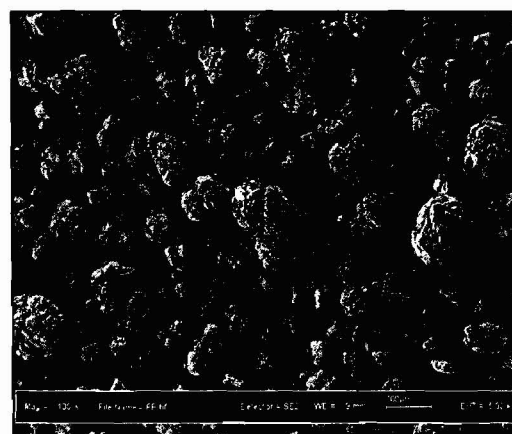
more small particles size of catalyst the greater potency it will poison compare to the particles size. This indicates why Pd catalyst is more active than Cu and Fe catalyst poisoned with sulphur.



**Figure 6** Particles distribution and size (0.002 mm) for Palladium catalyst



**Figure 7** Particles distribution and size (0.018 mm) for Copper catalyst



**Figure 8** Particles distribution and size (0.018 mm) for Iron catalyst

### 3.4.2 Nitrogen Adsorption (NA)

The surface areas of the catalysts were determined by nitrogen adsorption. The measured BET surface areas are done for all the fresh and poison catalyst samples. The surface of catalyst decreases for all the samples but not to the same extent, as seen in Table 2 below.

**Table 2** BET surface area

| Samples                                    | BET surface area, m <sup>2</sup> /g |
|--|-------------------------------------|
| Pd/Al <sub>2</sub> O <sub>3</sub> (fresh)  | 36.8526                             |
| Pd/Al <sub>2</sub> O <sub>3</sub> (poison) | 19.2253                             |
| Cu/Al <sub>2</sub> O <sub>3</sub> (fresh)  | 93.7130                             |
| Cu/Al <sub>2</sub> O <sub>3</sub> (poison) | 18.2376                             |
| Fe/Al <sub>2</sub> O <sub>3</sub> (fresh)  | 29.5368                             |
| Fe/Al <sub>2</sub> O <sub>3</sub> (poison) | -                                   |

Copper catalyst has greater surface area than Palladium and Iron catalyst in fresh condition, but after exposing into 10 ppm H<sub>2</sub>S, catalyst loss most its surface area. Palladium less lost its surface area compared to Copper and Iron catalyst. Adsorptions of Sulphur species inside the active sites reduce the amount of active sites for adsorption or dissociation of reactants. Sulphur species will cover the surface of catalyst, beside that it can produce metal-sulphur bonds

## 4.0 CONCLUSION

At high temperature catalytic combustion system, catalysts still achieve 100% methane conversion because the catalyst is self generated. Based on the results, Palladium catalyst is found to be most active catalysts for the combustion of methane and have high catalyst activities compared to Copper and Iron catalyst. If the catalyst have greater surface area higher activity resulting because greater surface areas were the reaction takes place and this will increase the catalyst activity. The present of sulphur in catalytic combustion can deactivate the catalyst activities, where reduce the catalyst activity beside reduce the surface areas of the catalyst. Nitrogen adsorption characterization shows that, all catalyst loss its surface areas when poisoned with sulphur. Local catalyst resources like Cu and Fe can be utilized in commercial utilization sector for high temperature application system for total oxidation process.

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