

## CATALYTIC COMBUSTION OF HYDROGEN AND METHANE FOR AUTOTHERMAL REFORMER START-UP IGNITION SYSTEM

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### ABSTRACT

Catalytic combustion is a phenomenon in which fuel and oxidant are completely oxidized on a catalytic surface. The interest in this process arises for two reasons: for pollution abatement and for energy generation. The objective of this research is to study the amount of heat produced from catalytic combustion system by adopting a bi-fuel concept: hydrogen and methane. The combustion of hydrogen is used to pre-heat the reactor to reach the ignition temperature of methane. The light off temperature of methane with air/CH<sub>4</sub> ratio of 5.3 is 368 °C. Platinum has been found as one of the catalyst that ignites hydrogen at room temperature. Once the ignition of methane is achieved, the flow of hydrogen is discontinued and replaced by methane.

**Keywords:** catalytic combustion; methane; hydrogen; catalyst; ignition temperature; platinum

### 1. INTRODUCTION

The catalytic combustion process has been extensively studied as an alternative process for energy production (Hayes and Kolaczkowski, 1997; Dupont et al. 2002; Seo et al, 1999; Minsker, 2000, Choudhary, 2002; Gelin And Primet, 2002). It was mostly used for small sized heaters in the early stage of the development. Today, it is becoming an increasingly viable technology in power generation, domestic heating appliances and chemical process heaters (Hayes and Kolaczkowski, 1997). Catalytic combustion has some advantages compared to the conventional combustion. Firstly, it has a lower lean limit of flammability than flame combustion. Even lean mixtures that cannot be burned by gas combustion can be burned by catalytic combustion. The adiabatic flame temperature decreases as a mixture becomes more lean. Therefore if the catalytic combustion is applied to any combustion system, it is possible to keep its flame temperature low enough to prevent production of thermal NO<sub>x</sub> (Dupont et al, 2002). Secondly, the light-off temperature of catalytic combustion is lower than the ignition temperature of gas combustion, because the activation energy much less than that for gas-phase reaction (Gelin And Primet, 2002; Sadamori et al, 1994). For example, gas combustion has ignition temperature of 615 °C for

methane, but catalytic combustion has a light-off temperature of below 400 °C even though it depends on the kind of catalyst and reaction condition employed.

Catalytic combustion of methane is somewhat more complicated because it is necessary to initiate oxidation at quite a high temperature. Once the reaction starts, subsequent oxidation is rapid and the heat release is considerable. In the case of catalytic combustion methane, the temperature of the combustion chamber need to increase before oxidation initiate at the ignition temperature for methane (Ozawa et al, 1994). For example, the light off temperature of methane with air/CH<sub>4</sub> ratio = 5.3 is 368 °C. Methane has an advantage over other fuels because the reaction takes place in complete combustion. It burning more cleanly, resulting in the production of smaller quantities of carbon dioxide and other pollutant. The capability of catalytic combustion which is operates at low temperature prevent formation of thermal NO<sub>x</sub> that occurs at high temperature, above 1500 °C.

Until recently, the necessary heat for start-up was provided from several sources such as electrical heater, pilot burner, igniter, hot exhaust gas and compressor (Moallemi et al, 1999; Dalla Betta et al, 1995; Mandai and Gora, 1995; Furuya et al, 1996). For example, automotive catalytic converters that use hot exhaust gas to preheat the converter during cold start process takes around 2 minutes before the temperature level reached (Kirhner and Eigenberger, 1996).

The objective of this paper is to introduce the concept of catalytic combustion of hydrogen to aid ignition temperature of methane without using any external devices. In this research, a catalytic burner has proposed as a heat supply system for the ATR reactor. The system is using a catalyst, which is platinum coated on monolith honeycomb surface in the catalytic burner. Hydrogen function to initiate combustion at room temperature (Deutschman et. al, 2000) and it act as a replacement for spark plug glow plug or electrical heater for started reaction. The experimental will run starts with a pure hydrogen/air flow through the catalyst in the reactor that is ignited catalytically. Then, the methane feed is slowly increased and at the same time hydrogen concentration will be reduce. Many paper and articles claim that ignition of hydrogen on platinum occurs at almost at room temperature but not many of them study extensively on the experiment.

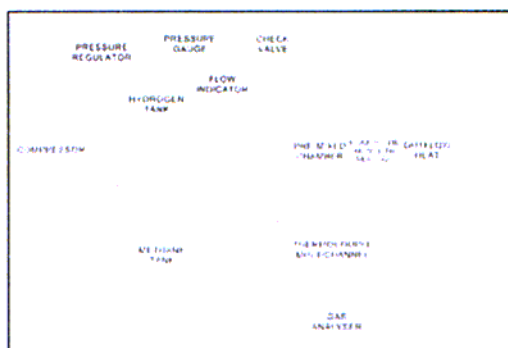


Figure 1. Experimental rig for catalytic combustion system

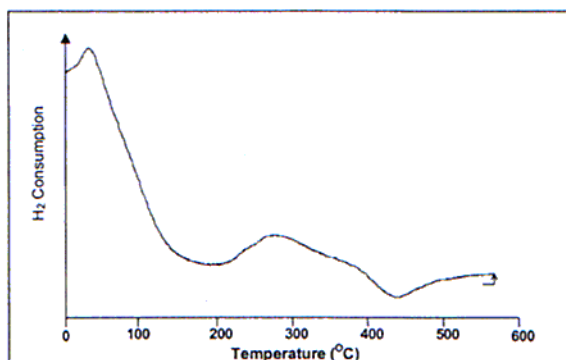


Figure 2. Temperature-programmed reduction of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst prepared

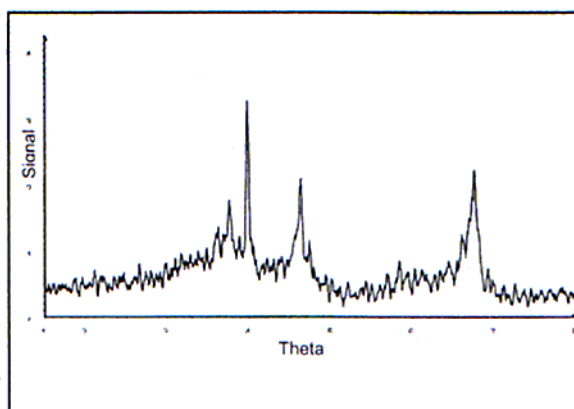


Figure 3. X-Ray Diffraction of 1 % Pt/Al<sub>2</sub>O<sub>3</sub> catalyst

## 2. EXPERIMENTAL

### 2.1. Catalyst preparation

Alumina supported catalysts were prepared by incipient wetness impregnation with aqueous solutions of hexachloroplatinic salt ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) followed by treatment in an oven at 110 °C for 12 hr. The catalyst was then heated at 500 °C for 8 hr for the calcined process. This calcined catalyst was then sieved to a 100 mesh size (particle diameters = 150  $\mu\text{m}$ ) to ensure uniform particulate size distribution.

### 2.2. Catalyst characterization

Characterization of the catalyst has been carried out by using a temperature programmed reduction (TPR) model Thermo Finnigan TPD/R/O 1100 and X-Ray diffraction (XRD) model Bruker XRD D8 Advance. The TPR analysis was carried out using a  $\text{H}_2$  (5%, v/v)  $\text{N}_2$  gaseous mixture having volumetric flow of 20 ml/min passing through 0.045 g of sample placed in a quartz reactor, heated at 10 °C/min from 40 °C to 450 °C.

In the XRD experiment, the powder catalyst placed in a sample holder plate is pressed with a glass slide to obtain a uniform distribution of powder. The diffractometer connected with a computer interface to measure the component deflection angle, which ranges between 15 – 80°. The diffraction pattern was analyzed by comparing with standard PDF file to determine the component within the sample.

### 3. RESULTS AND DISCUSSION

The existence of Pt/Al<sub>2</sub>O<sub>3</sub> was validated using the TPR and XRD characterization method. The temperature-programmed reduction (TPR) curve for Pt/Al<sub>2</sub>O<sub>3</sub> is shown in figure 2. The TPR profile of the Pt/Al<sub>2</sub>O<sub>3</sub> sample shows main reduction peaks with a maximum at 40 °C and 280 °C. These peaks can be related to the reduction of two Pt species, which are PtO and PtAl<sub>2</sub>O<sub>3</sub>. The peak in the initial region, present a maximum peak at 60 °C is identifying as PtO. This temperature reduction is following the range for their species below 50 °C (Hwang and Yeh, 1996). The second peak shows the maximum temperature reduction of Pt/Al<sub>2</sub>O<sub>3</sub> at 280 °C. This peak was in their range due to the temperature reduction that is depending on the type of metal precursor used. For example, Pt<sub>NH3</sub>/Al<sub>2</sub>O<sub>3</sub> presents a reduction maximum at 255 °C while Pt<sub>C14</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt<sub>C16</sub>/Al<sub>2</sub>O<sub>3</sub> present their maximum at 285 °C (Paulis et al, 2001).

The result from XRD experiment was depicted in figure 3 while the peaks assignment is tabulated in table 1. Five peaks were observed from XRD pattern with d value = 2.26, 1.96, 1.39, 2.39 and 1.92 Å. Four of these peak with d value =2.26, 1.96, 1.38 and 1.92 Å are identified as PtO, Pt and alumina peaks. Similar results were observed by Shen and Kawi (2003) and Cho et al (1997). The last peak was identify as PtO peak with d value = 2.39 Å. Both of these characterization were confirm this catalyst was prepared contain Pt/Al<sub>2</sub>O<sub>3</sub> and PtO.

**Table 1.** XRD peaks assignment for 1 % Pt/Al<sub>2</sub>O<sub>3</sub> catalyst

Sample	Temperature (°C) calcined	d-value	Peak assignment
Pt/Al <sub>2</sub> O <sub>3</sub>	500	2.26	Pt
		1.96	Pt
		1.38	Al <sub>2</sub> O <sub>3</sub>
		2.39	PtO
		1.91	Al <sub>2</sub> O <sub>3</sub>

### CURRENT RESEARCH STATUS

The catalyst sample for 1% Pt/Al<sub>2</sub>O<sub>3</sub> has already prepared and characterized. This catalyst will be tested on the test rig to study their performance and activity. Further step is to prepare this catalyst with different weight loading which are 3 and 5% Pt/Al<sub>2</sub>O<sub>3</sub>.

## REFERENCES

- Hwang, C.P. and Yeh, C.T., "Platinum-Oxide Species Formed By Oxidation of Platinum Crystallites Supported On Alumina." *Journal of Molecular Catalysis A: Chemical*, vol. 112, 1996, pp. 295-302.
- Moallemi, F., Batley, G., Dupont, V., Foster, T.J., Pourkashanian, M. and Williams, A., "Chemical Modelling and Measurements of the Catalytic Combustion of C4/Air Mixtures On Platinum And Palladium Catalysts." *Catalysis Today*, vol. 47, 1999, pp. 235-244.
- Furuya, T., Hayata, T., Yamanaka, S., Koezuka, J., Yoshine T and Ohkoshi, A., "Catalytic Combustion for Stationary Gas Turbine-Concept And Small Scale Test Result", ASME Paper 87-GT-99, Gas Turbine Conference And Exhibition, Anaheim, California, 1987.
- H. Sadamori, T. Tanioka and T. Matsuhisa, "Proceeding of the International Workshop on Catalytic Combustion" Tokyo, pp. 158-161, 1994.
- Cho, I.H., Park, S.B., Cho, S.J., and Ryoo, R., "Investigation of Pt/G-Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared by Sol-Gel Method: XAFS And Ethane Hydrogenolysis." *Journal of Catalysis*, vol. 173, 1998, pp. 295-303.
- Lee, J.H. and Trim, D.L., "Catalytic Combustion of Methane" *Fuel Processing Technology*, vol. 42, 1995, pp. 339-359.
- Minsker, L.K., Yuranov, I., Slavinskaia, E., Zaikovskii, V. and Renken, A., "Pt And Pd Supported on Glass Fibers as Effective Combustion Catalysts." *Catalysis Today* vol. 59, 2000, pp. 61-68.
- Paulis, M., Peyrard, H., and Montes, M., "Influence of Chlorine On The Activity and Stability of Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts in the Complete Oxidation of Toluene" *Journal of Catalysis*, vol. 199, 2001, pp. 30-40.
- Deutschman, O., Maier, L.I., Riedel, U., Stroemman, A.H., and Dibble, R.W., "Hydrogen Assisted Catalytic Combustion of Methane on Platinum." *Catalysis Today*, vol. 59, 2000, pp. 141-150.
- Gelin, P. and Michel Primet, M., "Complete Oxidation of Methane at Low Temperature over Noble Metal Based Catalyst: A Review." *Applied Catalysis B*, vol. 1023, 2002, pp.1-37.
- Hayes, R.E. and Kolaczkowski, S. T., "Introduction to Catalytic Combustion." *Gordon and Breach Science Publishers*, Amsterdam, , 1997.
- Betta, R.A.D., Schlatter, J.C., Yee, D.K., Loffler, D.G., and Shoji, T., "Catalytic Combustion Technology to Achieve Ultra Low Nox Emission: Catalyst Design and Performance Characteristic." *Catalysis Today*, vol. 26, 1995, pp. 329-335.
- Shen, S.C. and S. Kawi, S., "Selective Catalytic Reduction of NO by Hydrocarbons in the Presence of Excess Oxygen using Pt/MCM-41 Catalysts." *Applied Catalysis B*, vol. 45, 2003, pp. 63-76.
- Mandai, S. and Gora, T., "Study on Catalytically Ignited Premixed Combustion" *Catalysis Today*, vol.26, 1995, pp. 359-363.
- Kirhner, T. and Eigenberger, G., "Optimization of the Cold-Start Behaviour using an Electrically Heated Pre-Catalyst." *Chemical Engineering Science*, vol. 51, 1996, pp. 2409-2418.
- Choudhary, T.V., Banerjee, S. and Choudhary, V.R., "Catalyst for Combustion Methane and Lower Alkanes." *Applied Catalysis A*, vol. 234, 2002, pp. 1-23.
- Dupont, V., Zhang, S.H., Bently, R., and Williams, A., "Experimental and Modelling Studies of the Catalytic Combustion of Methane." *Fuel*, vol. 81, 2002, pp. 799 – 810.
- Ozawa, Y., Fujii, T., Kikumoto, S., Sato, M., and Fukuzawa, H., "Proceeding of The International Workshop on Catalytic Combustion." , Tokyo 1994, pp. 166-169.

Seo, Y.S., Kang, S.K., Han, M.H. and Baek, Y.S., "Development of a Catalytic Burner with Pd/Nio Catalysts." *Catalysis Today*, vol. 47, 1999, pp. 421-427.