

CHAPTER III EXPERIMENTAL

3.1 Materials

The idealite ceramic monolith used in this study was obtained from the US partnership collaboration of Prof. Daniel E. Resasco and also cut in the 2×2×15 mm³ rod prior to use. Gamma alumina (γ -Al₂O₃) purchased from Alfa[®]AESAR[®] (U.S.A) was ground using ball mill machine to obtain a particle size of around 5-10 μ m before being used as a washcoating material. Glacial acetic acid with a purity of 99.8% was purchased from Aldrich (Milwaukee, WI) for being used as a washcoating medium without further purification. Palladium (II) nitrate dehydrate [Pd(NO₃)₂·2H₂O] and lanthanum nitrate hexahydrate [La(NO₃)₃·6H₂O] of 99% purity were supplied from Fluka (Switzerland), and hexachloro platinic acid (H₂PtCl₆) with a purity of 99% was purchased from Carlo Erba (Milan, Italy) for being used as the active element precursors as received. Air zero grade, methane (CH₄), hydrogen (H₂) and nitrogen (N₂) with an ultra high purity used to investigate the catalytic activity of all catalysts were purchased from Thai Industrial Gases Co., Ltd.

3.2 Experimental Apparatus

3.2.1 Eight Tubular Flow Reactors System

The eight tubular flow reactor based on the concept of high-throughput screening apparatus was designed and constructed. It mainly consists of (i) gas mixing section, (ii) catalytic reactors, and (iii) analytical section, as shown in Figure 3.1.

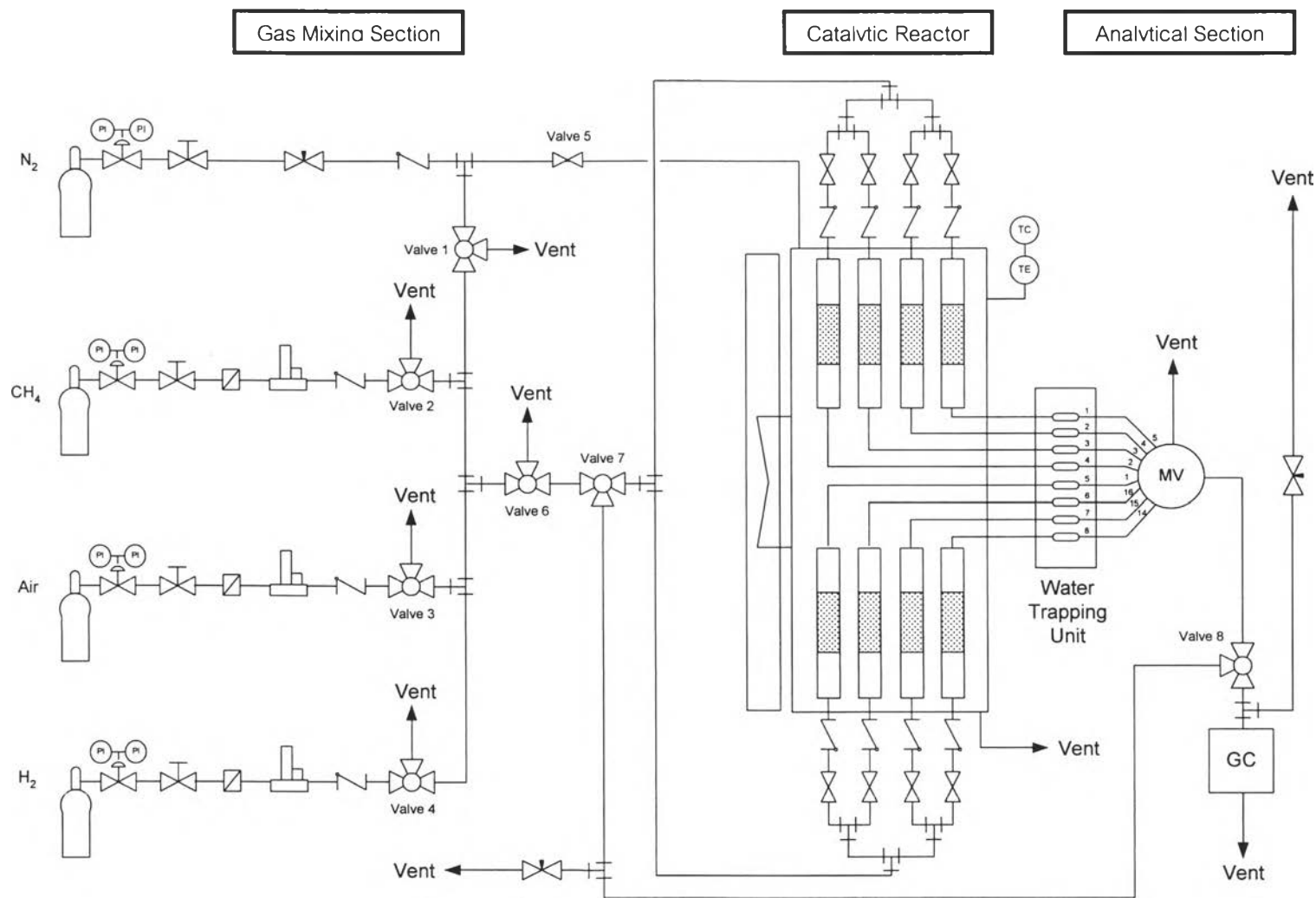


Figure 3.1 Schematic flow diagram of the eight tubular flow reactors equipped with GC.

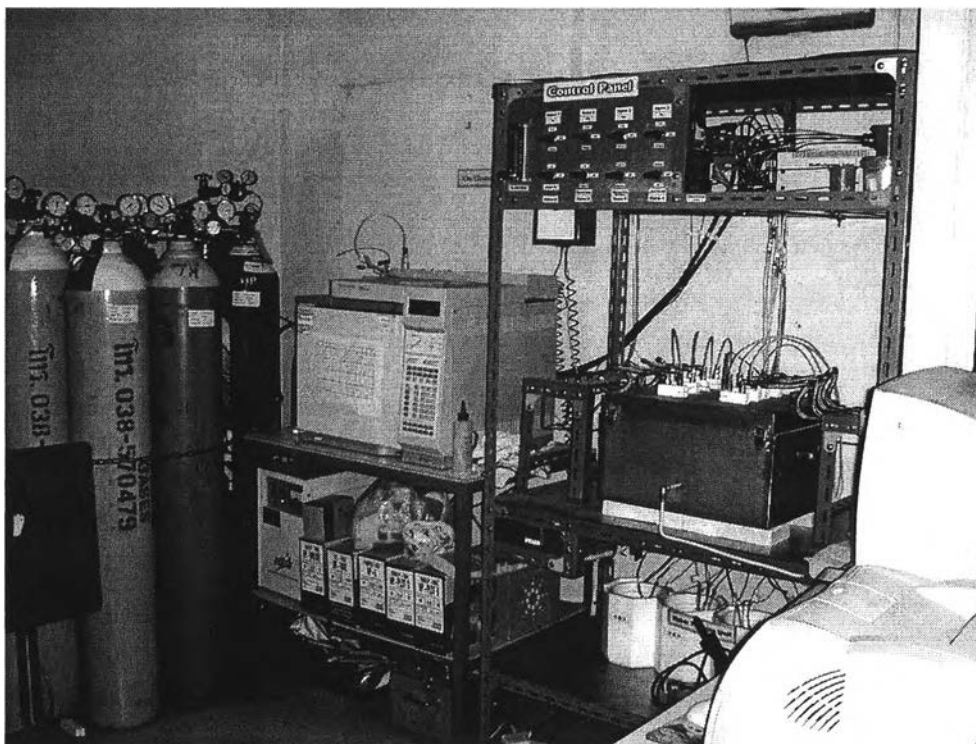


Figure 3.2 Reaction system photograph of the eight tubular flow reactors equipped with GC developed in this study.

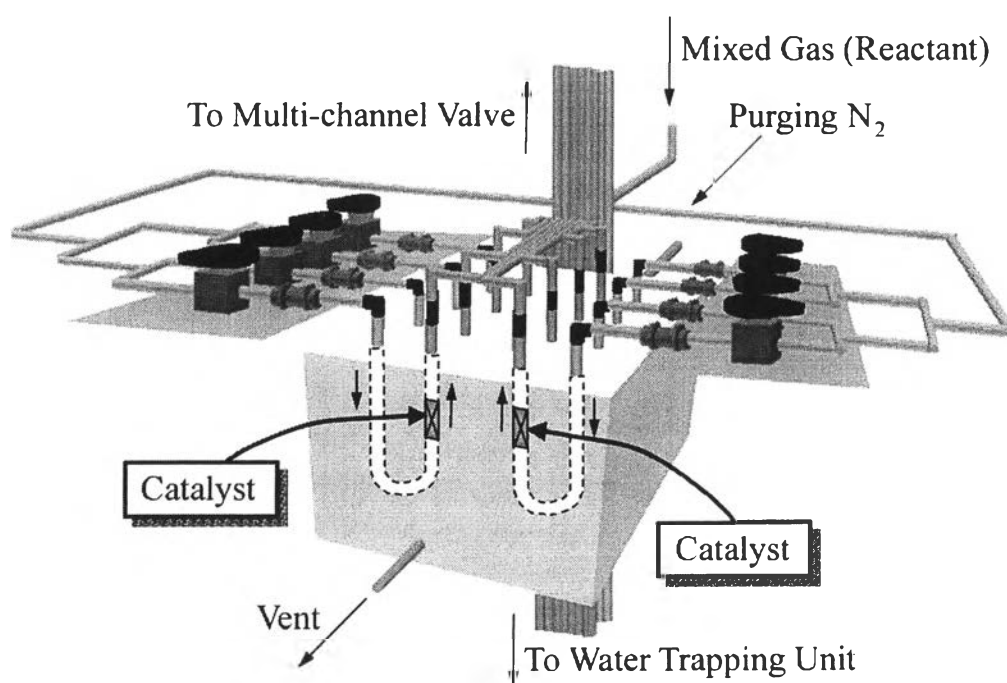


Figure 3.3 Portrait of the eight tubular flow reactors.

3.2.1.1 Gas Mixing Section

The reactant gas consisted of nitrogen, methane, air, and hydrogen. Nitrogen was used as a purge gas inside catalytic reactors and furnace to avoid the local temperature rise on catalyst and give a good thermal distribution inside furnace, respectively. Methane and air were used as reactant gases to perform catalytic combustion reaction. A constant flow rate of these two reactants were controlled by using gas mass flow controllers (GFC), AALBORG Instrument & Controls Inc., model GFC171S. Before entering GFC, these reactants must flow through 7 micron filters to trap the particles entrained in the gas that may damage GFC. Check valves with 1 psig cracking pressure were also installed after the GFC to prevent reverse flow. Hydrogen was used as a reducing agent to achieve a metallic state of some active elements before screening for their catalytic activity.

3.2.1.2 Catalytic Reactor

Stainless tube with ¼” outside diameter was used in the U-tube shape as a catalytic reactor since it provides a reactant-preheating zone. Eight of them were submerged into a furnace whose temperature was controlled by Maxthermo temperature controller model MC2438 equipped with K-type thermocouples. Purging nitrogen was also applied to ensure a good distribution of temperature inside the furnace. At the entrance of each reactor, 1 psig cracking pressure check valves were installed to prevent some reverse flow. Catalysts were packed inside the U-tubes between two layers of quartz wool used to hold the catalysts at the same position in each reactor.

3.2.1.3 Analytical Section

Water trapping unit was installed to condense the water in the flue gases to avoid some corrosion problem and also prevent some damage to GC column. Eight streams from the reactors flowed through a multi-channel valve aiming to select only one stream to analyze with GC at a time. After the sampling gas was passed into GC column, the multi-channel valve selected another stream sent to GC, serving for the next analyzing cycle, and the cycle were repeated until all of the eight streams were analyzed along time-on-stream.

3.2.2 Analytical Instrument

The selected stream from the multi-channel valve was analyzed by using Hewlett Packard 6890N gas chromatograph. Two capillary columns were used in series with a switching valve controlling the analyzed gas flow to each column as programmed for the separation of all components. HP-PLOT Q with 20 μm coating thickness, 0.32 mm I.D. and 30 m length was firstly used for separating CO_2 and CH_4 from the gas mixture while HP-MOLSIV with 25 μm coating thickness, 0.32 mm I.D. and 30 m length was subsequently used for separating the other species. Each cycle of GC analysis took around 8 min to complete before starting the next injection. The conditions of GC are listed as follows:

Injector Temperature:	100°C
Oven Temperature:	
- Initial time:	63°C
- At 1.00 to 7.17 min:	68°C
- Final time:	63°C
TCD Conditions:	
- Temperature	200°C
- Reference gas	N_2 (99.99% purity)
Carrier Gas:	He (99.99% purity)
- Flow rate:	2.2 mL/min

3.3 Catalysts Preparation Procedure

3.3.1 Monolith Washcoating

Dried monoliths were dipped into 2.5% (wt) acetic acid solution for around 2 min to make rougher surface and also rinsed with DI water until the acid was leached out. After that, they were dried at 110°C until the weight remained constant before being dipped into 40% (w/v) γ -alumina slurry (in 2.5% acetic acid) for around 10 seconds. The excess slurry in monolithic channels was sucked out by the suction pump. The dipping procedure was repeated for 10 times before calcining at 500°C for 3 hrs. The washcoated thickness was examined and confirmed by SEM.

3.3.2 Library I: Catalysts for Studying the Effect of Calcination Step

Two calcination methods were performed to study the effect of calcination step related to the alumina phase. In the first method, washcoated monoliths were dried over night and calcined at 500°C for 3 hrs before impregnation with a mixture solution of active elements to achieve 5% of total loading. After that, they were calcined again at 900°C with the same holding time before being investigated for their catalytic activity. The second method was quite the same, except the temperature in the first calcination step being changed to 900°C. The phase transformation of γ -Al₂O₃ due to calcinations were monitored by XRD. The catalytic activity results gave a decision to select the appropriate condition for the further studies.

3.3.3 Library II: Catalysts for Studying the Effect of Loading Amount

Palladium was selected to be the representative active element for this test since it has a highest combustion activity. Eight catalysts, which contained different loading amounts of Pd, were prepared with the appropriate preparation condition from the previous test by incipient wetness method in order to study the effect of loading amount. The catalytic activity results also gave a decision to select the appropriate loading amount for the further studies.

3.3.4 Library III: Catalysts for Studying the Effect of Using Pd, Pt and La in mono-, bi-, and tri-elements System

The appropriate preparation condition and loading amount from the previous experiments were used to generate a library of catalysts. Palladium, platinum, and lanthanum were co-loaded in mono-, bi-, and tri-element system according to tertiary diagram. All active element solutions were homogeneously mixed before impregnation. The amounts of three elements in each catalyst were varied simultaneously by a 20% interval, which resulted in 21 catalyst members in the library. The steady state catalytic activity results were used to construct some contour plots at different temperatures, aiming to indicate the active zone and also select some lead formulations.

3.4 Catalytic Activity Screening

Heterogeneous combustion of methane was performed in the eight tubular flow reactors. Eight prepared monolithic catalysts at a time were packed inside the U-tubes before being reduced at 600°C with H₂ for 1 hour. After that, inert nitrogen gas was switched to flush out some remaining hydrogen and also used to avoid the hot spot during the change of temperature to a new set point of the testing temperature. 2% methane in air with 1 m/s linear velocity was passed through the reactors to start the reaction when the temperature was reached the set point. The first cycle of GC analysis was started after 15 min left and also continued until all of catalysts were screened their catalytic activity for 7 time-on-streams (around 8 hrs). Both conversion and selectivity were calculated and reported in Appendix A.

3.5 Catalyst Characterizations

3.5.1 X-ray Diffraction (XRD)

Powder x-ray diffraction (XRD) patterns were investigated on Rigkagu X-ray diffractometer system equipped with a Rint 2000 wide-angle goniometer using CuK α radiation with a generator voltage and generator current of 40 kV and 30 mA, respectively. The goniometer parameters were: divergence slit = 1°(2 θ), scattering slit = 1°(2 θ), and receiving slit = 0.3 mm. The catalyst samples were ground and packed on a glass holder. Scan speed of 5° (2 θ)/min with a scan step of 0.02° (2 θ) was used during a continuous run in the 10° to 90° (2 θ) range. The digital output of proportional X-ray diffractor and the goniometer angle measurements were transferred to an online microcomputer to record data and subsequent analysis.

3.5.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) experiments were performed on the JEOL 5200, with the magnification of 35-200,000. The SEM provides unique information about the washcoated thickness and also the surface morphology of materials, which are the catalysts for the present research. Samples were stuck on the

stubs and coated with gold by ion sputtering device (JFC-1100E) for 4 min in order to prevent specimen charging. The examinations were taken through this microscope with a magnification ranges from 50 to 700.

3.5.3 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) patterns were collected with TPDRO machine (Thermo Electron: TPDRO 1100) equipped with Quadrupole Mass Spectrometer (QMS) to observe some oxygen desorption behavior from the active elements. Lead formulations were packed in the TPDRO sample cell before being placed in the sample holder of TPDRO machine. Heating rate employed was 10°C/min starting from 100 to 900°C. Thermal conductive detector (TCD), which transferred data online to computer, were employed to detect and send some oxygen releasing signal versus catalyst temperature. Two type of detectors, Faraday Cup and Scanning Electron Multiplier (SEM), were used to confirm the oxygen signal from TCD by monitoring the species contained $m/z = 32$ along testing time. The results from TCD and MS were compared each other in order to evaluate only the oxygen signal versus catalyst temperature.