

## CHAPTER II

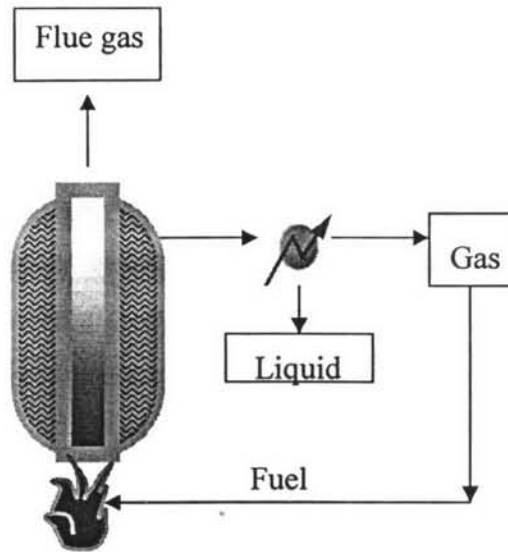
### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Pyrolysis

Pyrolysis has been proposed as a viable recycling technology to treat the very large tonnages of used tires. Pyrolysis, the thermal degradation of the rubber of the tire using heat at high temperatures (450-700°C) in the absence of oxygen, produces oil, char, gas and residual steel products. Three phases are obtained after tire pyrolysis, which are solid (47-63% char), liquid (30-43% water and oils), and gas (2.4-4.4% light hydrocarbon: H<sub>2</sub>, CO, and CO<sub>2</sub>). Product distribution and composition have also recently been studied as a function of the thermal treatment (Berrueco *et al.*, 2005).

Since most tires contain sulphur from the vulcanization process, the pyrolysis of waste tires also produces hydrogen sulphide in additions to hydrocarbons. This hydrogen sulphide also entrains with the light hydrocarbon stream, that is generally used as fuel, and thus, is eventually converted to SO<sub>x</sub> during combustion. Proper disposal of the pyrolyzed gas stream before exhausting is very crucial to avoid the subsequent environmental problems created from the processed gases.

The utilization of gaseous products obtained from tire pyrolysis as a fuel to provide thermal energy to the process as shown in Figure 2.1 can lead to higher benefits. However, some pollutants formed during the combustion of pyrolysis gas also create subsequent emission problems, which are necessary to be abated before exhausting.



**Figure 2.1** Schematic flow diagram of a typical tire pyrolysis utilizing gaseous products as a fuel to supply thermal energy to the process.

The flue gas exhausted to the atmosphere from the process consists of HC,  $\text{SO}_x$ ,  $\text{NO}_x$ , CO and  $\text{CO}_2$ , which are pollutants, and they can subsequently create emission problems. Catalytic combustion is an interesting alternative to effectively treat those emissions before exhausting.

## 2.2 Fuel Combustion

Combustion is a burning process in which the fuel is heated above its ignition temperature in the presence of oxygen. If complete combustion takes place, the elements carbon (C), hydrocarbon (H), and sulphur (S) react with the oxygen contained in air, forming carbon dioxide ( $\text{CO}_2$ ), water vapor ( $\text{H}_2\text{O}$ ), and sulphur dioxide ( $\text{SO}_2$ ), respectively. When there is not enough oxygen present or the fuel/air mixture is not sufficient, the burning gases are partially cooled below their ignition temperatures, and the combustion process remains incomplete. The flue gases then contain burnable components, mainly carbon monoxide (CO), carbon (C), and various hydrocarbons ( $\text{C}_x\text{H}_y$ ), that are, along with  $\text{NO}_x$ , pollutants which harm our environment.

## 2.3 Catalytic Combustion

Catalytic combustion is an interesting alternative for the abatement of organic pollutants at low temperature. Catalysts have become useful for helping volatile organic compounds (VOCs) and hydrogen to react with oxygen to form less environmentally harmful carbon dioxide and water.

### 2.3.1 Methane Oxidation Catalysts

The active metals used for catalyzing a complete oxidation of methane can be divided into two groups: noble metals and transition metal oxides. Both families of catalysts have been extensively studied to develop catalytic combustion applications (Muller *et al.*, 1996; Widjaja *et al.*, 1999 and Sekizawa *et al.*, 2000).

The main advantage of noble metals over metal oxides is their higher specific activity, which makes them the best for low-temperature combustion of hydrocarbons.

#### 2.3.1.1 *Low Temperature Catalytic Combustion (LTCC)*

Low Temperature Catalytic Combustion (LTCC) is applicable in the temperature range of 300-500°C to eliminate trace volatile organic chemicals (VOCs) in the air and residual hydrocarbons or other organic compounds in the chemical and petrochemical process streams.

The most-used elements for the application are noble metals, such as palladium (Pd) and platinum (Pt). However, due to the high cost of noble metals, using transition metals is becoming more attractive today.

### 2.3.2 Palladium-based Catalysts

Noble metals display exceptional catalytic activity in the combustion of hydrocarbons. Thus, the activity of Pd-based catalysts in light hydrocarbon combustion has been studied for many years.

Palladium (Pd) catalysts are generally accepted as the most active catalyst commercially available for the oxidation of unsaturated and saturated

hydrocarbons with less than five carbon atoms, particularly for methane. It is used in many applications, such as in the combustion of natural gas and in the abatement of pollutants using the catalytic combustion technique due to the following properties (Centi, 2001): (1) higher activity on methane combustion, which results in a low light-off temperature as has been recognized for a long time; (2) the unique capability of temperature self-control associated with the PdO-Pd reversible transformation; and, (3) the low volatility of the Pd species (metal, oxides, hydroxides, and oxyhydroxides) under thermal and hydrothermal conditions.

Palladium (Pd)-supported alumina has been reported for its excellent methane combustion activity. Two different forms of PdO were suggested to have a higher combustion activity when compared with its dispersed form. The thin layer of PdO covering on a metallic Pd core was observed to activate methane combustion by Oh *et al.* (1991), while the PdO dispersed on a metallic Pd cluster was suggested by Datye *et al.* (2000).

The main disadvantage of using Pd is that it is easily deteriorated with a small amount of sulphur in the fuel, such as natural gas or a tire pyrolyzed gas stream (Hoyos *et al.*, 1993). Lee and Trium (1995) found that the activity of Pd can be thermally destroyed by sulphate group adsorption either under vacuum or under nitrogen. The activation energy of palladium catalysts poisoned with SO<sub>2</sub> increased in which is consistent with the transformation of active PdO sites to less active PdO-SO<sub>x</sub> sites.

Many studies have been accomplished on Pd supported in various ways, and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been reported as the best catalyst (Sekizawa *et al.*, 2000). However, using zeolite is also attractive since some studies reported higher dispersion and activity of PdO achieved from Pd-supported H-ZSM5 and H-mordenite catalysts (Montes de Correa *et al.*, 1996). In addition, zeolite acidity plays an important role in the CH<sub>4</sub> oxidation reaction. The acid-base property of the support surfaces could affect the strength of Pd-O bonds in the PdO<sub>x</sub> species (Okumura *et al.*, 2003). In general, the more basic the support surfaces, the easier it is for the O species on the surfaces to donate electrons to the Pd atoms, thus creating the stronger Pd-O bonds, which results in higher temperatures for oxygen desorption and CH<sub>4</sub> reduction of the supported Pd catalysts. On the other hand, acidic support is preferred for a Pd-

supported catalyst since it can weaken the bond strength of Pd-O, resulting in higher oxidation activity (Shi *et al.*, 2003).

The addition of a promoter into Pd-based catalysts can also help catalysts to improve their activity. The addition of Zr to Pd/HZSM-5 can promote low temperature oxidation of the catalyst (Shi *et al.*, 2003). In contrast, the additions of strong basic metal oxides, such as Cu, La, Ba, Fe, Mn, Ca, Mg, and Li, decreases total conversion capabilities for CH<sub>4</sub> combustion. The addition of TiO<sub>2</sub> on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts was also investigated (Wang *et al.*, 2002), and it was found to weaken the bond strength of Pd-O, thus promoting this oxygen to react easily with methane as compared to the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, Fraga and coworkers (2004) studied the addition of La and Sn to alumina-supported Pd catalysts for methane combustion. Their results suggested that PdO interaction with Sn species did not allow PdO crystal growth.

## 2.4 ITQ-21 Zeolite

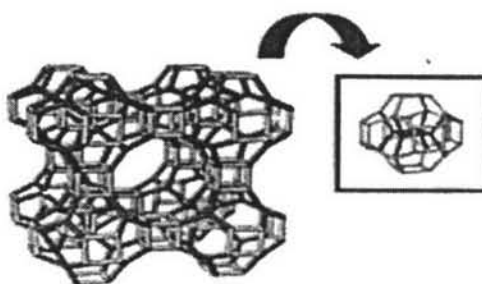
Zeolites are interesting oxidation catalysts. The exchanged metal in the ionic state can also be stabilized, thus providing high dispersion of the active components. Moreover, the acidity of zeolites can also create activated molecular oxygen, forming peroxide species. Molecular oxygen has been proposed to adsorb on the weak Lewis acid sites and increase the electron deficiency of the sites (Kalantar Neyestanaki *et al.*, 2002). The species can withdraw electrons from hydrocarbons and oxidize them. The presence of a strong hydrogenating function provided by the noble metal allows almost complete hydrogenation of the aromatic molecules under mild conditions.

Zeolite is also an especially suitable material for the investigation of the support effect because it is easy to control the amount and the strength of acid sites through changing Al concentration and structure.

Recently, ITQ-21 (Institute de Tecnología Química number 21) is a new tridimensional large pore zeolite in which its calcined state has the chemical composition given by the equation;



by  $(n+m)$  is at least 5 until 7, where X is a trivalent element, Z is Ge, Y is at least one tetravalent element other than Ge, and the ratio  $m/(n+m)$  is between 0.0 to 0.5 (Arribas *et al.*, 2004). ITQ-21 has been successfully synthesized by using an N(16)-methylsparteinium cation in combination with fluoride anions and germanium. This zeolite contains, as in faujasite, large cavities about 1.18 nm diameter, which are accessible through six circular 12 membering (12MR) windows 0.74 nm wide. A view of the unit cell of ITQ-21 is shown in Figure 2.2.



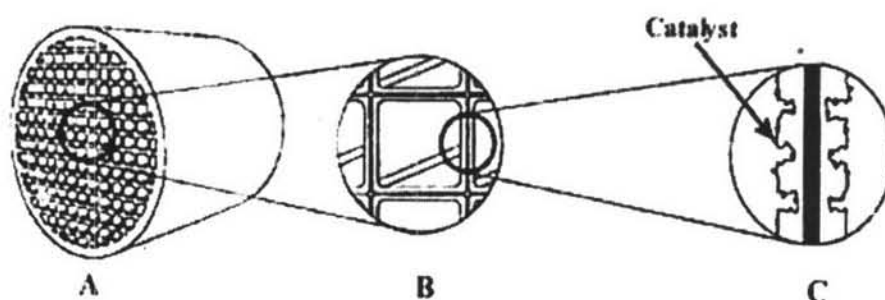
**Figure 2.2** Perspective view of the structure of ITQ-21 zeolite (Arribas *et al.*, 2004).

The structure of this zeolite is stable when heated at temperatures higher than 700°C, and is able to support acid sites in the framework. The presence of the acid sites and the widely-open structure of this zeolite is expected it to produce a better quality gasoline from pyrolysis of large molecules. This can be received from a combination of two zeolite characteristics within ITQ-21, Y and ZSM-5, which is expected to better promote Pd dispersion, oxidation activity, and stability of Pd-O. In this research, it was expected that the interaction between the acid sites of ITQ-21 and PdO can prevent PdO from sintering and maintain the appropriate size of PdO during the reaction.

## 2.5 Monolithic Catalysts

Monolithic honeycomb catalysts have been used with increasing frequency due to their characteristics of a very low pressure drop at elevated mass throughput, high geometrical area, and mechanical strength (Climino *et al.*, 2001 and Heck *et al.*,

2001). The monolith structure is normally ceramic, but may be metallic, and it acts as a substrate for a washcoat slurry of base metals required on catalytic materials. The monolithic catalyst consists of a structure of parallel channels with walls coated by a porous support with catalytically active particles (See Figure 2.3).



**Figure 2.3** Illustration of a honeycomb monolithic catalyst (Philippe *et al.*, 1999).

## 2.6 Combinatorial Approach

The combinatorial approach including high-speed chemical synthesis, high-throughput screening, high-capacity information processing is an alternative to create, analyze, and interpret large numbers of new and diverse material compositions. The technology has now been being developed to make this powerful integration possible (McFarland and Weinberg, 1999).

Combinatorial chemistry and high throughput experimentation can present a new technology in chemistry. This technology offers a shorter time to prepare and test many samples in a single experiment, thus requiring lower cost for research and development. This technology, therefore, is rapidly entering industrial laboratories (Scheidtmann *et al.* 2001).

Halzwarth *et al.* (2001) have suggested that this combinatorial approach can be categorized in two complementary methodologies: primary and secondary screening. Primary screening deals with the discovery of new materials via the systematic exploration of combinations of elements for the preparation of multi-component materials. The screening techniques typically used for primary screening are scanning mass spectroscopy and infrared thermography. A multi-flow reactor has

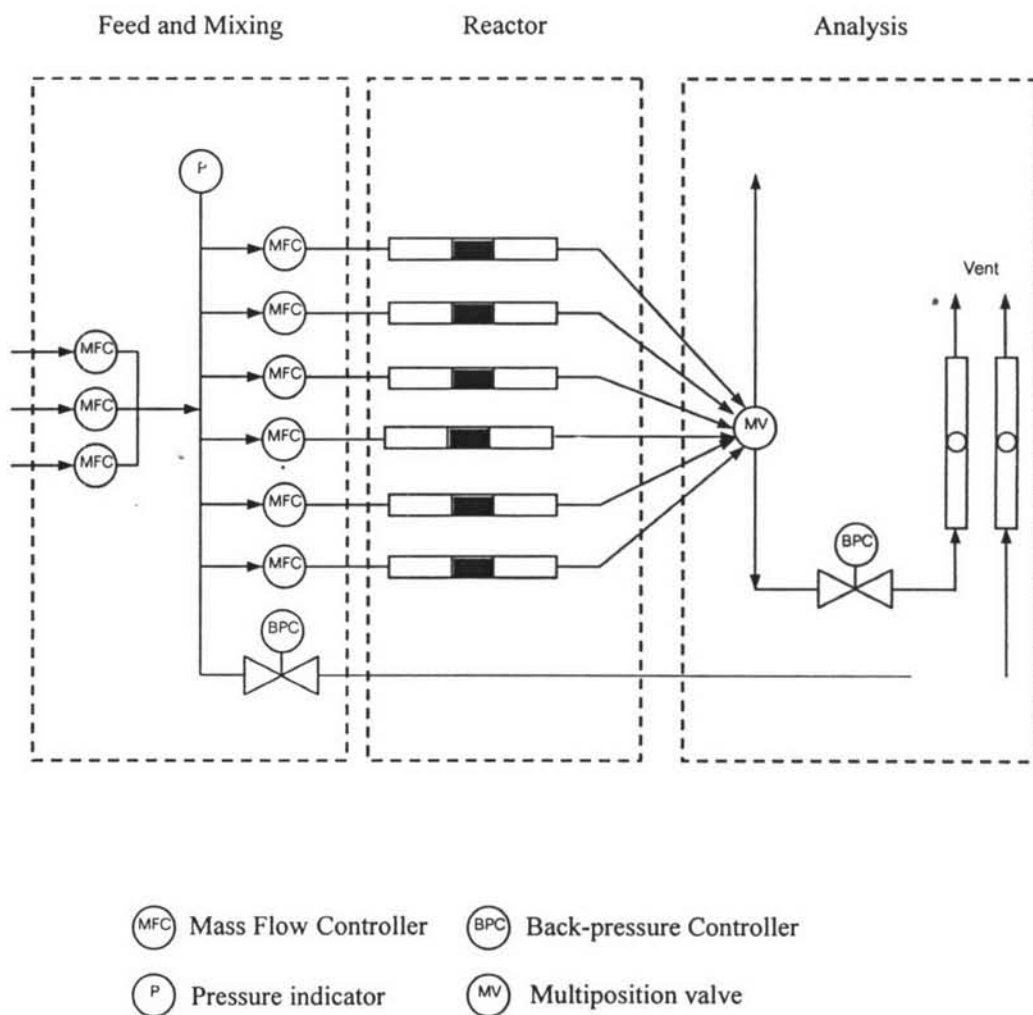
also been successfully used for the primary screening (Pérez-Ramírez *et al.*, 2000 and Kraikul *et al.*, 2005). Secondary screening targets the optimization of already-existing formulations. High-throughput preparation and evaluation of materials under conditions are the important characteristics of this second methodology, which are usually considerably slower than primary screening techniques due to the more accurate and detailed information needed. This screening can be achieved by employing continuous parallel flow micro-reactors with the identification of reaction products.

A combination of primary and secondary screening has been proposed to be the most effective approach, because new materials discovered by primary screening can subsequently be optimized by secondary screening.

## 2.7 High-Throughput Screening

High-throughput method is an attractive way to screen catalyst formulation in rapid fashion. The basic principle of the six-flow reactor successfully applied in catalyst testings and kinetic studies is similar to that of the single-flow reactor system, as seen in Figure 2.4. Different sections can be distinguished as: a gas mixing section, a reactor section, and an analysis section. Table 2.1 summarizes the past and current catalytic systems, which have already been studied and developed.





**Figure 2.4** Schematic flow-sheet of the six-flow reactor system for fast catalyst screening and kinetics studies (Pérez-Ramírez *et al.*, 2000).

**Table 2.1** Utilization of the six-flow technology in catalyst development: screenings and kinetic study (Pérez-Ramírez *et al.*, 2000)

Process	Catalytic System	Product Analysis
CO oxidation NO <sub>x</sub> reduction with CO Water shift reaction	Cu/Cr/activated carbon Cu/Cr/activated carbon Cu/Cr/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> Cu/Cr/activated carbon	} GC NO <sub>x</sub> -analyzer
NO <sub>x</sub> reduction with ammonia	Cu/Cr/activated carbon Mn oxides/activated carbon Mn oxides/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> Modified activated carbon Mn <sub>2</sub> O <sub>3</sub> -WO <sub>3</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	} MS
Soot oxidation	Ag/Mn/ZrO <sub>2</sub> Cu-V/ Al <sub>2</sub> O <sub>3</sub> Cu/K/Mo/(Cl)/ ZrO <sub>2</sub> Cu/K/Mo/(Cl)/ TiO <sub>2</sub> Cu/ZrO <sub>2</sub> Mo/ ZrO <sub>2</sub> V/ ZrO <sub>2</sub> Cs <sub>2</sub> MoO <sub>4</sub> -V <sub>2</sub> O <sub>5</sub> CsVO <sub>3</sub> -MoO <sub>3</sub> Cs <sub>2</sub> SO <sub>4</sub> -V <sub>2</sub> O <sub>5</sub>	} NDRI HC-analyzer
Chlorofluorocarbon (CFC) hydrogenolysis	[Rh, Ru, Re, Pt, Pd, Ir]/ activated carbon Pd/ activated carbon Pd-zeolite Y Pd-mordenite	} GC NO <sub>x</sub> -analyzer
N <sub>2</sub> O decomposition NO <sub>x</sub> reduction with hydrocarbon	Calcined hydrotalcites (Co, Pd, La, Rh) [Fe, Co, Rh, Rd]-ZSM-5 Pt/Al <sub>2</sub> O <sub>3</sub> Pt-ZSM-5	} GC NO <sub>x</sub> -analyzer
Fischer-Tropsch synthesis	Co-zeolite Y Co/SiO <sub>2</sub>	} GC

GC: Gas Chromatography; NO<sub>x</sub>: Nitrogen Oxides; MS: Mass Spectrometer; HC: Hydrocarbon  
NDIR: Non-Dispersive InfraRed.