

CHAPTER II

LITERATURE SURVEY

2.1 Background

The combustion of toxic or malodorous compounds present in gaseous process emissions is an accepted air pollution control technique. Catalytic combustion, also known as catalytic oxidation, is the essentially complete chemical reaction of a gaseous compound with oxygen when both are in contact with a solid material as called catalyst that increases the rate of the reaction. The catalytic combustion of volatile organic compounds can be applied in order to limit emissions of such vapors and protect air from pollution. This method is potentially advantage because it can operate at lower temperatures than thermal combustion. Use of oxidation catalysts permits to decrease the temperatures to obtain complete combustion of the organic compounds. The lowering of reaction temperatures leads to several advantages in terms of environmental impact as well energy saving, low production of pollutants and reduction of fuel costs. Gas-phase combustion can only occur within given flammability limits, and the temperatures produced during combustion can rise to above 1600 °C, where the direct combustion of nitrogen and oxygen to unwanted nitrogen oxides can occur. Catalytic combustion offers an alternative means of producing energy. A wide range of concentrations of VOCs can be oxidized over a suitable catalyst, and it is possible to work outside the flammability limits of fuel. Reaction conditions can usually be controlled more precisely, with reaction temperatures being maintained below 1600 °C. This may be important both to minimize the production of nitrogen oxides and also to avoid thermal sintering of the catalyst (Lee and Trimm, 1995). Fig. 2.1 illustrates the general pattern of activity curve in the catalytic combustion of various hydrocarbons. As

temperature is increased, oxidation is initiated at a temperature that depends on types of hydrocarbon and catalyst. A further increase in temperature leads to an exponential increase in rate (area B) to the point where heat generated by combustion is much greater than heat supplied. The reaction becomes mass transfer controlled (area C) until the reactants are depleted (area D).

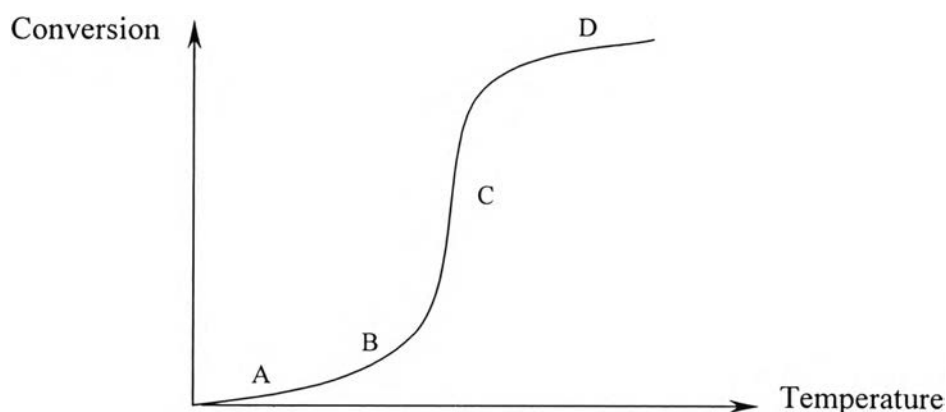


Fig. 2.1 Conversion as a function of temperature in catalytic combustion.

One important factor in the catalytic combustion of hydrocarbons is “light-off temperature”. The catalytic activity in terms of light-off temperature can be defined as the minimum temperature for measurable catalyzed conversion occurred, and is dependent on the chemical properties of the catalyst. According to the conversion curve as shown in Fig. 2.1, the definition of light-off temperature is the temperature at which conversion reaches 10%, 20%, or 50% depends on the definition in each case. The lowest light-off temperature, the most active catalyst ought to be chosen to enhance catalytic combustion at the lower temperatures and leads to considerably economical advantages for heat requirement. It is also seen that the kinetics of catalytic combustion is only relevant to parts A and B of Fig. 2.1. Once light off occurs, mass and heat transfer are the important parameters. The geometry of the catalytic combustor together with the porosity of the catalyst support has much

more effect in this region. The reaction rapidly approaches complete conversion and the heat generated from the combustion results in a significant increase in catalyst temperature. Hence, the stability of catalysts at high temperatures is also of considerable interest. Thus, it is clear that considerations of catalytic combustion must include the chemical reactivity of the catalyst and the hydrocarbon (area A and B), mass and heat transfer effects (area C) and the maximum temperature reaches (relevant to area D). Catalytic combustion of volatile organic compounds has long been studied. The use or improvement of catalytic processes, including catalytic combustion, has a number of applications with regard to the future design of utility.

The catalytic destruction of halogenated air toxins and the effect of admixture with VOCs have been studied (Windawi and Zhang, 1996). Supported platinum group metal catalysts have been successfully commercialized for complete destruction of environmentally harmful halogenated volatile organic compounds. Catalyst composition and organic species was formed to control the light-off characteristics. The light-off temperatures were 200 °C lower on a titania-based catalyst than on an alumina-based catalyst. Unsaturated chlorocarbons are more stable than saturated ones and the temperatures of activation for oxidation of unsaturated hydrocarbons are lower than saturated ones.

Catalytic oxidation of four organic compounds, n-butanol, n-butyraldehyde, n-butyric acid and toluene, was studied on four commercially available catalysts consisting of 0.1% platinum, 0.5% platinum, 0.5% palladium, and 10% copper oxide supported on γ -alumina (Wasfi *et al.*, 1978). The reaction was carried out at reactor inlet temperatures ranging from 116 °C to 497 °C, with space velocities of 50,000, 80,000, and 100,000 hr⁻¹. The platinum catalysts were found to be more effective in terms of chemical conversion whereas the palladium and copper oxide catalysts required much higher temperatures than the platinum catalysts for comparable performance.

The catalytic oxidation of 40 to 250 ppm trichloroethylene (TCE) in air was evaluated over 1.5 % Pt/ γ -Al₂O₃ on a cordierite monolith with 62 cells per cm² in the temperature range 150 to 550 °C with space velocities of 1,000 to 30,000 hr⁻¹ (Wang *et al.*, 1991). Over 99.9 % conversion of TCE was achieved at 30,000 hr⁻¹ and 550 °C with fresh catalyst. The main products from the oxidation of TCE are CO₂, HCl, and Cl₂. However, trace amounts of chlorinated hydrocarbon product (C₂Cl₄) and CO as intermediate products are also found. The addition of 1.5 vol % water or 0.6 vol % methane to the feed promoted the complete conversion of chlorine to HCl and decrease the rate of production of byproduct perchloroethylene.

The catalyst can be used in any configuration or size that sufficiently express the catalyst to the gas stream being treated. Metal oxides and noble metals such as Pt, Pd, and Rh have been used as catalysts for the catalytic oxidation of volatile organic compounds. Noble metal catalysts show higher activity than metal oxide catalysts (Spivey, 1997). They can be used either with or without a support, but supported catalysts are favorable for oxidation. One particular advantage of supported metal catalysts is that the metal can be dispersed over a high surface area of the support and shows greater activity than the unsupported metal catalysts due to interactions of the metal with the support. The support also reduces thermal degradation. The application of noble metals other than Pt and Pd in catalytic combustion is limited practically because of their high volatility, ease of oxidation and limited supply (Lee and Trimm, 1995). Noble metals are usually dispersed on a support in order to stabilize thermally the catalyst and, in some cases, may be involved in the catalytic reaction. For catalytic combustion, where high throughputs are required, the catalyst is often suspended in a washcoat and on a substrate. Both compounds have several roles to play. Several types of substrates may be used including pellets, wires, tubes, fibre pads and monoliths.

2.2 Catalytic Combustion of Nitrogenated Volatile Organic Compounds

Nitrogenated volatile organic compounds, referred to herein as VNCs, such as amines and nitrile, must be removed from industrial off-gas streams prior to venting the gas stream into the atmosphere. Amines, when present in waste gas streams, are classified as compounds causing an odor nuisance. Typical emission sources for amines include pharmaceuticals manufacture, especially synthetic polymer spinning; tanning processes; agriculture and fish processing; and municipal sewage services. Some of the most common easiest available nitrogenated volatile organic compounds are ethylamines. Diethylamine (DEA) is recommended for the synthesis of rubber-processing chemicals, such as metal salts of diethyldithiocarbamate and tetraethylthiuram disulfide. This amine is also employed in the preparation of insecticides, insect repellants, dyestuffs, and corrosion inhibitor. These compounds thus have the potential of being present in the wide range of VOCs emissions either as a pure component or as part of a mixture (McKetta and Cunninkam, 1997).

Catalytic combustion process for destruction of VNCs has the advantage of operating at much lower temperatures than thermal combustion process and thus remove the mechanism to generate thermal NO_x . However, there is still the potential to produce chemical NO_x due to the nitrogen associated with the VNCs. The process involves passing a gas stream containing VNCs plus an oxidizing agent, such as air, through a reactor consisting of the catalyst. The flow rate through the system should be sufficient to allow for conversion greater than at least 90% and preferable greater than 95% destruction of the VNCs without any other undesirable compounds of interest. Thus, the gas hourly space velocity (GSHV) can vary significantly over a range of 1,000 to about 300,000 hr^{-1} and preferably over a range of 5,000 to 60,000 hr^{-1} (Rossin and Campell., 1998). The process

described according to above is also applicable to the injection of fluid nitrogenated volatile organic compounds into a gas stream consisting of inert compounds plus an oxidizing agent. The gas stream containing the vaporized nitrogenated volatile organic compounds is then contacted with the catalyst. The reaction temperature range within operating condition is based on a number of factors. They include the conversion of the target VNCs to be decomposed, the reactivity level of the target VNCs, the space velocity and the percentage of the noble or base metal associated with the catalyst. Generally, the low operating temperatures are used for catalytic combustion of VNCs in the presence of relatively low concentrations in the incoming gas stream less than about 500 ppm for example (Rossin and Campell., 1998). Further, decreasing the space velocity of the incoming gas stream and/or increasing the percentage of the base or noble metal component associated with the catalyst may reduce the operating temperature. It should be noted that since oxidation reactions of the VNCs are exothermic, the temperature of the incoming gas stream to be treated should be adjusted to take into account the potential for the reaction temperature at the catalyst bed. The temperature should not be increased exceed the amount of heat required by the chemical reaction so that the catalyst temperature does not enhance the NO_x formation significantly. In case of diethylamine which is used as a model compound for this present study, the heat requirement for complete combustion is 36.71 kcal/mole.

Extensive research has been carried out on the oxidation mechanisms of various inorganic, hydrocarbon, and oxygenated/halogenated hydrocarbon compounds. However, very little data, either mechanistic or kinetic, are available on the fate of nitrogenated volatile organic compounds in combustion operating at high temperature or with a catalyst. Thermal combustion and catalytic combustion are two destructive methods that may be used for controlling off-gas emissions. Thermal combustion of off-gas streams containing VNCs generates both thermal and chemical nitrogen dioxide (NO_2)

and nitric oxide (NO), herein referred to collectively as NO_x, which are the most prevalent forms of nitrogen oxide. NO_x are present in measurable quantities in the atmosphere. Thermally generated NO_x gases are the result of the oxidation of nitrogen (N₂) and occur at high operating temperatures, while chemically generated NO_x gases result from chemical reactions involving the atomic nitrogen associated with nitrogenated volatile organic compounds. It is well known that NO_x is a leading constituent of toxic compounds, smog, and acid rain. Further, they have been linked to depletion of stratospheric ozone. While these gases are produced from natural sources, man-made sources can result in higher than desirable concentrations and therefore control of these emissions is desirable. The use of thermal combustion to decompose VNCs requires a costly NO_x abatement process to be employed to control their emissions.

The oxidation of monoethylamine (MEA) over Pd-monolith catalysts has been studied (Borgharkar and Abraham, 1994). Palladium plays a more significant role as an active site for C-N bond splitting and oxidation to CO₂ and water. Palladium supported on alumina shows the ability for complete oxidation to CO₂, N₂, and H₂O. The effect of nickel oxide as an additive to palladium supported on alumina was also studied. Reactivity to complete oxidation products was determined as Pd + alumina > Pd + NiO + alumina > alumina. Alumina was primarily responsible for MEA adsorption and dehydrogenation.

Apparently the most successful catalyst used for selective oxidation of VNCs is a copper-exchange zeolite (Kuwabara *et al.*, 1992). The catalytic removal of triethylamine by selective oxidation to N₂, CO₂, and H₂O was carried out on a copper-exchange zeolite over the temperature range 523-673 K. The selectivity to N₂ was 92 % and the formation of NO_x was less than 5 ppm with the reactant concentrations of 8,000 ppm of (CH₃)₃N with 21 vol % O₂. Trace amounts of N₂O product were also found at 673 K. However, such a catalyst is subjected to poisoning by sulfur and halogen compounds often

found in industrial off-gas streams. Further, crystalline zeolite molecular sieve is relatively costly to prepare for industrial applications.

There is a report of the catalytic combustion of a number of VNCs over a proprietary supported platinum monolithic catalyst on behalf of Allied Signal, Inc. This report has been presented at 1993 Meeting of the American Chemical Society in Denver Colorado (Lester and Homeyer, 1993). The Pt-based catalyst was supported on a 400 cells per in² coming cordierite substrate. This catalyst was able to readily destroy the VNCs tested, however, very significant quantities of NO_x were generated. Therefore, use of this catalyst in a process to destroy VNCs would also require an additional abatement treatment of NO_x gases.

The present invention relates to a catalytic combustion process for oxidatively decomposing VNCs without producing significant amounts of NO_x emissions. The process of the present invention comprises catalytically oxidizing VNCs using a catalyst, which includes a noble or based metal, deposited on a catalyst support comprising zirconia or titania and promoted by additions of vanadium molybdenum or tungsten in the presence of an oxidizing agent. Lanthanum is a preferred addition for thermal stabilization of the catalyst. More particularly, a gaseous stream containing one or more VNCs is passed through a catalyst bed at a selected temperature range to obtain a complete oxidation, which selectively produce CO₂, H₂O, N₂, N₂O, respectively. The complete combustion products such as N₂, CO₂, and H₂O are always found at low temperatures, approximately less than 400 °C, whereas N₂O is usually detected at moderate temperatures. Trace amounts of 127 ppm of N₂O was found at 450 °C according to the catalytic oxidation of hydrogen cyanide on a catalyst which was prepared containing 1% palladium, 5% vanadium, and 5% lanthanum supported on titania (Rossin and Campell, 1998). The process may be operated at temperatures ranging from about 200 to 500 °C depending upon the particular composition of the catalyst, the

residence time, and the particular constituents present in the incoming gas stream as well as their concentrations.

The process according to the present invention employs a catalyst composition, which comprises a noble or a based metal supported on titania (TiO_2) or zirconia (ZrO_2) and may be promoted with selected amount of molybdenum (Mo), tungsten (W), or vanadium (V). These catalyzed compositions have been discovered to possess the ability to effectively destroy VNCs in oxidation reactions without generating significant NO_x emissions over selected relatively low temperature ranges (Rossin and Campell, 1998). In general, effective catalyst compositions contain about 0.03 to 5% of a noble metal or about 0.1 to 10% of a based metal, which is impregnated onto either a titania or zirconia support. Adding molybdenum, tungsten, or vanadium as a promoter of the selective oxidation reaction and lanthanum (La) is preferred addition to promote thermal stability of the catalyst and appears to enhance the selectivity towards the formation of nitrogen among the combustion products. All percentages of catalyst components expressed herein are on a weight basis of the total formulation unless otherwise specially designated. Preferable, the titania or zirconia support possesses a high surface area to obtain better dispersion of the components of the catalyst. The catalyst may be configured in many typical and well-known forms, such as pellets, granules, rings, spheres, cylinders, or it may take the form of a coating on an inert carrier, such as monoliths. Monolithic catalysts are being extensively used in the control of automobile emissions, as well as in many existing VOCs emission control strategies.

2.3 Monolith Catalyst

Monolith catalysts are mainly used for catalytic combustion in order to obtain high geometric areas of the catalyst and lower pressure drop through the system. The choice of monolith material is made on the basis of physical

and chemical properties such as surface area, porosity, thermal stability and conductivity, reactivity with reactants or products, chemical stability, and catalytic activity. For catalytic combustion, a high surface area is required. Hence, there is a need to increase the low surface areas of the monolith structure. This can be achieved by covering the substrates with a porous layer of ceramic material, which is called a washcoat. The washcoat is coated on the substrates to provide a high surface area. The thermal expansion coefficient of washcoat should be similar to that of the substrate, since a large difference may result in washcoat-substrate separation. Furthermore, the surface area of washcoat should not be changed under operating conditions since a decrease in the surface area (e.g. caused by sintering) can result in pore closure and encapsulation of active catalytic sites. Fig. 2.2 shows the conceptual model for catalytic sites dispersed on a high surface area Al_2O_3 carrier bonded to a monolith (Heck *et al.*, 1989). The number and diameter of the channels determine the amount of geometric surface area, which the washcoat is deposited. There is a limit to how much washcoat can be deposited, since too many results in a decrease of the effective channel diameter, thereby increasing the pressure drop to an unacceptable level.

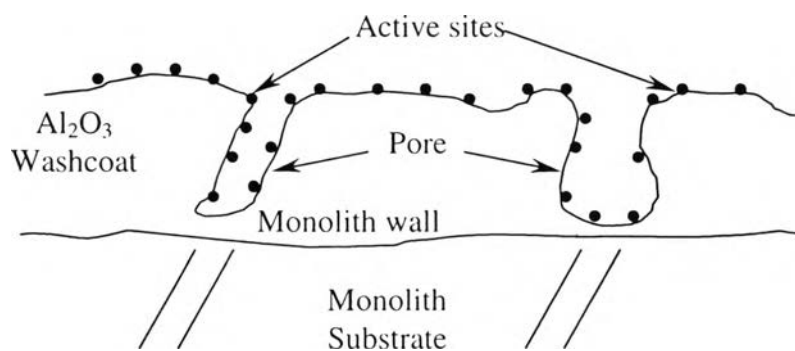


Fig. 2.2 Model for catalytic sites dispersed on a monolith catalyst.

For the commercial-honeycombed monolith catalyst, a variety of cell shapes and sizes can be manufactured. The cell densities can be varied and normally are available from 10 to 600 cells per square inch (cpsi). The pores in the cell walls are relatively large and the surface area is typically in the range of 0.1 to 1.0 m²/g. For use in catalysis, the passageways or channels are usually coated with the high surface area carrier, as called alumina washcoat, which provides a stable and high surface area for catalyst dispersion to increase the effective surface area to the range of 20 to 50 m²/g (Satterfield, 1991). The honeycombed-monolithic form may be preferred when it is desired to reduce the pressure drop through the system or minimize attrition or dusting. If a monolith form of the catalyst is desired, a slurry or solution of titania, zirconia, titania plus promoters, or zirconia plus promoters may be first coated onto the monolith wall by means well known to the art. The noble or based metal can be added in any convenient manner to the other components, but preferably is added last using well-known conventional means to accomplish uniform impregnation of the metal onto the coated monolith support. In addition to use in the control of VOCs emissions, the monolithic catalysts have also been widely used both already implemented into common practice and still at the developmental stage in the industrial technologies.

The UOP precious supported metal catalysts on washcoat cordierite monolith were studied for the oxidation of VOCs and halogenated VOCs (Noordally *et al.*, 1993). The low-temperature and high-temperature oxidation catalysts showed high destructive efficiencies and excellent stability when CO and various hydrocarbon emissions were treated to form CO₂ and H₂O. While the halogenated hydrocarbon oxidation catalyst is stable and highly active in destroying halogenated hydrocarbon to form CO₂, H₂O, and halogen acid.

The catalytic oxidation of trichloroethane (TCE) was carried out over PdO catalyst on γ -alumina (Yu *et al.*, 1991). The catalyst was 4% PdO/ γ -Al₂O₃ on 62 cells/cm² cordierite monolith catalyst. The products formed from the

catalytic oxidation of TCE were HCl, Cl₂, and CCl₄. Methane and water enhance TCE oxidation at lower temperatures, improve selectivity to HCl, and reduce production of CCl₄ and Cl₂. On the assumption that TCE oxidation obeys a first order and the activation energy was found to be 34 kcal/mole.

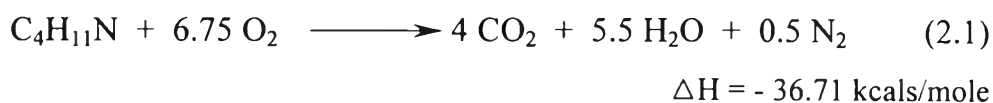
2.4 Kinetics of Heterogeneous Catalytic Combustion

The overall process of any catalytic reaction is a combination of mass-transfer, describing transport of reactants and products to and from the interior of a solid catalyst, and chemical reaction kinetics, describing chemical reaction sequences on the catalyst surface. The most cost-effective catalytic oxidation systems require use of a solid catalyst material having a high specific surface area. The presence of many small pores necessarily introduces pore transport diffusion resistance as a factor in the overall, or global kinetics. The overall process consists of the following steps: (1) transport of reactants from the bulk fluid through the gas film boundary layer to the surface of the catalyst particle; (2) transport of reactants into the catalyst particle by diffusion through the catalyst pores; (3) chemical adsorption of at least one reactant on the catalyst surface; (4) chemical reaction between chemisorbed species or between a chemisorbed species and a physisorbed or fluid phase reactant; (5) desorption of reaction products from the catalyst surface; (6) diffusive transport of products through the catalyst pores from the surface of the catalyst particle; and (7) mass transfer of products through the exterior gas film to the bulk fluid (Satterfield, 1991).

In principle, any of these above steps or some combination can be the rate-controlling step. In practice, temperature plays a primary role in determining the rate-controlling step. Any comprehensive analysis of actual catalytic oxidation systems of practical interest must include a quantitative understanding of the relative effects of mass transfer and surface reaction. The kinetic models for catalytic oxidation can either be mechanistic, a general

theory of the above mechanisms for the complete heterogeneous catalytic oxidation of low molecular weight organic vapors at trace concentrations, or empirical model. In case of an empirical equation, the model is a power law rate equation that express the rate as a product of a rate constant and the reactant concentrations raised to a power.

For catalytic combustion of nitrogenated volatile organic compounds such as diethylamine (DEA), the general reaction can be proposed as follow:



can be represented by the rate equation in term of the rate of CO₂ production

$$r_{\text{CO}_2} = k C_{\text{DEA}}^m C_{\text{O}_2}^n \quad (2.2)$$

The algebraic equation that relates r_{CO_2} to the species concentrations is called the kinetic expression or rate law. For a heterogeneous system, the reaction rate is based on mass of solid rather than on reactor volume because the amount of catalyst is important to the rate of reaction. For the conditions encountered in most VOC control applications, the concentration of oxygen will always be much larger than the concentration of the organic reactant. Thus, because the oxygen partial pressure will be essentially constant during the reaction, the observed rate will depend only on the concentration of VOC. For this reason, the reaction order with respect to oxygen was observed to be close to zero. On the other hand, the reaction order with respect to the VOC was always positive with values in the 0-1 range (Papaethimiou *et al.*, 1997).

The catalytic removal of trimethylamine by selective oxidation decomposition to N₂, CO₂, and H₂O was studied (Kuwabara *et al.*, 1992). They found that the reaction order with respect to the pressure of (CH₃)₃N was about 0.7 over 7.9 wt% Cu-Y Zeolites, whereas the order with respect to O₂

pressure was zero order in the range of above 10 vol% of O₂ over Cu-Y Zeolites at 573 K.