CHAPTER II

LITERATURE SURVEY

Emissions of volatile organic compounds (VOCs) are a concern in solvent-intensive operations in many manufacturing processes. Gaseous effluents and contaminated exhaust air containing VOCs enter the atmosphere, where they contribute to environmental pollution. Incineration is an energy efficient method to destroy VOCs. Such a process involves contacting the waste gas stream with a catalyst in the presence of excess oxygen at a temperature higher than 700°C depending on the nature of the VOCs. However, thermal incineration is very energy intensive and requires expensive materials of construction to withstand corrosion and high temperatures. Therefore, in order to reduce capital investments and fuel costs, there is a need for development of a catalyst, which can oxidize VOCs at lower temperatures. Research in the heterogeneous catalytic oxidation of low concentration of VOCs with air must focus on identifying highly active catalysts and obtaining environmentally benign reaction products at lower temperatures. In general, reaction conditions are chosen that result in complete oxidation to obtain the desirable end products of H_2O and CO_2.

The heterogeneous catalytic oxidation for controlling VOCs was reviewed by Spivey (1987). The most common catalysts used for VOCs abatement are metals or metal oxides such as Pt, Pd, Rh, and V_2O_5 dispersed on high surface area supports such as Al_2O_3, SiO_2, TiO_2, etc. Supported platinum is one of the most widely used catalysts for gases containing hydrocarbon and oxygenated hydrocarbons. However, platinum catalysts are susceptible to poisoning by chlorinated hydrocarbons. Bimetallic catalysts containing platinum and either palladium or rhodium find application in harsh reaction environments, such as automotive exhaust control, where the temperatures and space velocities tend to be very high. Although there have been many previous Pt catalyst studies, the adsorption, desorption, and reaction of VOC molecules on Pt has not been widely investigated. Hinz et al. (2001) studied propane oxidation in the absence and presence of SO_2 in the feed gas over 1%Pt on γ-Al_2O_3 using transient experiment with TAP (temporal analysis of products) and in

situ DRIFT spectroscopy. Without SO_2 in the feed gas, propane reacts consecutively in the sequence of propane to propene to ethane to CO to CO_2. In the presence of SO_2 the first step of the main route is the breaking of a C-C bond in propane producing ethane and a C_1 fragment, which then form CO and eventually CO_2. It was suggested that the promoting effect by SO_2 on the conversion of propane is due to the formation of an acidic site at the $Pt/Al_2O_3/SO_4^{2-}$ interface. Paulis *et al.* (2001) investigated the effect of chlorine, added either as a part of the platinum precursor salt or after the noble metal impregnation, on the catalytic activity of Pt/Al_2O_3 for complete oxidation of toluene. They prepared the Pt/Al_2O_3 catalysts from three precursors; $Pt(NH_3)_4(OH)_2$, $(NH_4)_2PtCl_4$, and $(NH_4)_2PtCl_6$. The measured catalytic activity sequence is as follows: Pt_{NH3}/Al_2O_3 > Pt_{Cl4}/Al_2O_3 > Pt_{Cl6}/Al_2O_3. Pt_{NH3}/Al_2O_3 showed an unchanged activity during the stability test. They also found that the H_2O formed during toluene oxidation had been reported as being responsible for Cl mobilization. The subsequent chlorine elimination by H_2O formed in the reaction will produce an increase of the activity.

Adding tin to platinum catalysts has proven to be beneficial for activity maintenance in applications such as catalytic reforming. One of the factors, which effect the interaction of tin and platinum, is the catalyst preparation method. Sexton *et al.* (1984) found that the catalyst prepared by coprecipitation of Sn with alumina followed by impregnation of platinum achieved the maximum contact between Pt and ionic tin. This catalyst also had a uniform distribution of both species of Pt and Sn. Moreover, it gave the highest activity and selectivity in methycyclopentane and cyclohexane conversion. Dautzenberg *et al.* (1980) observed that the sequence of metal impregnation is an important factor at a low tin content. They concluded that the modification of Pt-Sn alloy is more important than the effect of interaction of Pt with a tin(oxide)-modified support.

Baronetti and coworkers (1985) used three different preparation techniques for $Pt-Sn/Al_2O_3$ catalysts and characterized the samples by diffuse reflectance spectroscopy and temperature programmed reduction. Their results indicated that there was a strong interaction between Pt and Sn in the catalysts prepared by coimpregnation and sequential impregnation with Pt first, where a complex of $(PtCl_2(SnCl_3)_2)^{2-}$ was deposited on the alumina surface. However, when the catalysts

were prepared by sequential impregnation with Sn first, the complex formation did not occur, and only Pt(IV) and Sn(IV) species were observed on the alumina surface. The TPR profile of a sequentially impregnated catalyst was similar to the sum of TPR profiles of the two monometallic samples ($Pt/Al_2O_3+Sn/Al_2O_3$). They explained that Sn(II) deposited during the first impregnation was oxidized to Sn(IV) in the drying step, thereby preventing the formation of the $(PtCl_2(SnCl_3)_2)^{2-}$ complex when Pt(IV) was added as the second component, due to the weak interaction between $(PtCl_6)^{2-}$ and $(SnCl_6)^{2-}$ species.

Many research groups have worked on the characterization of the state of Sn, using various characterization methods such as chemisorption by static or pulse techniques (Lieske et al., 1983, Lieske and Völter, 1984, Wilson and Hall, 1979, Muller et al.,1979, Otter and Dautzenberg, 1978) , X-ray diffraction (XRD) (Srinivasan et al., 1987), X-ray photoelectron spectroscopy (XPS) (Sexton et al., 1984, Balakrishnan and Schwank, 1991, Adkins and Davis, 1984), Mössbauer spectroscopy (Li et al., 1991, Bacaud et al., 1981), temperature programmed reduction (TPR) (Sachdev and Schwank, 1988, Burch, 1981), etc. Srinivasan and coworkers, (1987) observed alloy formation with a Pt/Sn stoichiometry of 1:1 by using in-situ X-ray diffraction. Li et al. (1991) used Mössbauer spectroscopy to characterize the Pt/Sn catalysts. They found that the fraction of Pt present in an alloy phase increased with increasing tin content, and an alloy richer in Sn than Pt/Sn =1:1 was present on the silica support. Static chemisorption of hydrogen and oxygen was used for investigating the surface of catalysts by several investigators. For example, Otter and Dautzenberg (1978) studied the effect of hydrogen treatment at high temperatures (>500°C) on Pt/Al_2O_3. They attributed the decreasing amount of hydrogen chemisorption after reduction at a high temperature to the presence of highly dispersed platinum particles forming an alloy with the alumina support. Muller et al. (1979) observed that the amount of oxygen adsorption on the Pt-Sn bimetallic catalysts was proportional to both the percentages of platinum and tin on the alumina support. They found no evidence for the metallic state of Sn or Pt-Sn alloys.

Prior electron microscopy investigations of supported bimetallic catalysts have provided useful information about particle size distribution and elemental

composition of small regions. In an electron microdiffraction study of supported Pt-Sn catalysts, a Pt-Sn alloy with a 1:1 atomic ratio was observed (Srinivasan *et al.*, 1987). The results of X-ray photoelectron spectroscopy and temperature programmed reduction experiments showed tin to be in an average oxidation state of +2 (Burch, 1981, Baronetti *et al.*, 1985, Sexton *et al.*, 1984). In-situ x-ray diffraction revealed the formation of the PtSn alloy after a hydrogen reduction treatment at 500°C for 6 hours (Srinivasan *et al.*, 1987). Examination of Pt-Sn catalysts by Mössbauer spectroscopy has also confirmed the presence of alloys (Bacaud *et al.*, 1981).

The current state-of-the-art in VOC oxidation catalysis leaves room for improvement, both from a macroscopic process perspective as well as from the fundamental atomic and mechanistic aspects of surface catalysis and materials development. There is a dearth of fundamental studies of VOC catalysis, especially with regard to surface interactions of VOC molecules with metal catalyst surfaces. Important insights may be gained from systematically exploring the behavior of VOC catalysts by means of temperature-programmed methods such as temperature-programmed desorption (TPD) or reaction (TPR). A typical TPD experiment involves adsorption of the adsorbate(s) on a clean surface followed by a subsequent desorption of the adsorbate(s) and possible decomposition products as the temperature of the surface is increased.

Analytical techniques relating some characteristic property of the sample to its temperature in the course of a temperature-programmed heating process are commonly included in the field of thermal analysis (Lemaitre *et al.*, 1984). The characteristic temperature at which a thermal change will occur in a given sample will depend on the nature of the system under study (phase composition of the sample and composition of the surrounding atmosphere) and on any factors affecting the kinetics of the transformation. Some of the kinetic factors are related to the experimental arrangement used for thermal analysis (flow rate of gaseous reactants, effectiveness of heat and mass transfer between the solid and its surroundings, temperature program), while others are related to the solid sample itself (particle size, pore structure, state of dispersion in an inert material, presence of trace impurities, crystallinity). The interpretation of a thermogram is, therefore, fairly complex.

As a result of the remarks above, thermal analysis may be useful at two different levels:

1.   As a tool for both qualitative and quantitative analysis.

2.   As a way of evaluating the influence of various factors on the reactivity of a known substance.

The identification of the constituents in a sample is usually made by comparing its thermogram with that of a reference material, obtained under the same experimental conditions. This procedure has been used satisfactorily in many mineralogical studies. It will be effective for all sample consisting of mixtures of phases exhibiting a small degree of variation in their thermal behavior, as a function of secondary characteristics such as particle size, crystallinity, presence of trace impurities, and the like. The Temperature-Programmed Desorption (TPD) method has been used in many studies. A mathematical analysis of second-order temperature-programmed desorption spectra in the case of freely occurring redesorption was studied by Konvalinka et al. (1977). The use of equations relating the temperature of the peak maxima to the enthalpies of adsorption, both for first-order and second-order desorption kinetics, was critically evaluated. The shapes of the theoretical lines describing second-order desorption at several values of enthalpy of adsorption and initial coverage were calculated. Miller et al. (1993) studied the temperature-programmed desorption of hydrogen on supported platinum catalysts after hydrogen reduction at 300, 450, and $650^{\circ}C$. For all catalysts, reversible desorption of chemisorbed hydrogen occurred at approximately $175^{\circ}C$. It was suggested that the irreversibility of the spillover hydrogen results from dehydroxylation of the support at high temperature.

Verbeek and Sachtler (1976) investigated the surface composition of alloys of platinum and tin by adsorption and temperature programmed desorption (TPD) of deuterium and carbon monoxide. Based on TPD results, they referred to the ligand effect, which caused weakening of the chemisorptive bond of deuterium and carbon monoxide when the proportion of tin in the alloys increased. Davies and Mariotti (1996) showed the results of temperature-programmed desorption (TPD) of methanol on Cu(110) surfaces. They proposed that the reaction pathway was sensitive to the

local structure of the methoxy/oxygen adlayer and also confirmed the presence of two states of methoxy at the $Cu(110)/O(a)$ surface and assigned them to methoxy species with and without stabilization by surface oxygen. Farneth *et al.* (1985) showed the results of partial oxidation of methanol over MoO_3. Their values of the number of active sites and of the Arrhenius parameters for the rate-limiting C-H bond cleavage, both obtained by TPD under high vacuum with simultaneous microbalance and mass spectrometry detection, were used to predict heterogeneous reaction rates in excellent agreement with the reaction data. The decomposition and oxidation of methanol on Al_2O_3, Pd/Al_2O_3 and PdO/Al_2O_3 were studied by TPD and TPO (Temperature Programmed Oxidation) by Cordi and Falconer (1996). They observed that methanol decomposed undergoing both dehydrogenation and dehydration even on the blank Kaiser A-201 Al_2O_3 support which had been dehydrated and oxidized in $3\%O_2$ at 873 K for 10 min prior to TPD experiments. The main decomposition products of methanol were H_2 and CO, which came off around 600-900 K with maximum peak temperature at 780 K. On Pd/Al_2O_3, methanol decomposed to form H_2 and CO between 400-700 K, with at maximum peak temperature of 500 K. The Pd surface area was 3.3 m^2/g, which is much less than the alumina surface area of 200 m^2/g. This indicated that methanol adsorbed on the alumina, and migrated via surface diffusion to the Pd sites where it decomposed with a rate much higher than that on Al_2O_3.

Methanol has been widely used to represent VOCs in VOC oxidation studies since it has a simple chemical structure containing only carbon, hydrogen and oxygen atoms. It has been known that oxidation of methanol can give various products such as formaldehyde or CO_2 depending on types of catalysts and operational conditions. Yao *et al.* (2000) studied the kinetics of methanol oxidation over SiO_2 in the temperature range of 400-600 °C to investigate the oxidation partway of methanol. They found that methanol was first oxidized to formaldehyde, and then oxidized to CO. CO_2 was produced mainly from the oxidation of intermediate species products from dehydrogenation of formaldehyde on SiO_2.

Yields of methanol oxidation are also utilized as an intermediate in the synthesis of commercial chemical products such as formaldehyde, methyl formate or as a fuel, hydrogen. Cheng (1996) found that on MoO_3, the partial oxidation of

methanol to formaldehyde with high selectively is caused by water and methanol blocking the adsorption sites of formaldehyde. IR results have shown that formaldehyde, methanol, and water compete for the same adsorption sites. Therefore, formaldehyde cannot be further oxidized to carbon dioxide once the sites are occupied by methanol and water. Busca *et al.* (1987) conducted flow reactor studies by using FT-IR spectroscopy to reveal the mechanism of the selective oxidation of methanol to formaldehyde, dimethoxymethane, formic acid, and methyl formate over vanadium oxide and titanium oxide catalysts, which were prepared by impregnation and coprecipitation. Niwa and Igarashi (1999) studied the role of solid acids over MoO_3 loaded on SnO_2 in the selective oxidation of methanol to formaldehyde. They found that methanol was adsorbed more weakly on the acid sites than on exposed surface of SnO_2 resulting in the formation of formaldehyde. Elmi and coworkers (1989) concluded that the ability of coprecipitated vanadium-titanium oxide to catalyze the formation of methyl formate is correlated to the existence of dioxymethylene species with an intermediate stability as compared to pure titania and vanadia. Hydrogen production from partial oxidation of methanol on ZnO and ZrO_2 supported Pd catalysts was studied by Cubeiro and Fierro (1998). The results have clearly shown that Pd catalysts can compete with the commercial low temperature methanol synthesis $Cu/ZnO(Al_2O_3)$ catalysts when used under conditions of the partial oxidation of methanol.

The electrochemical oxidation of methanol is also widely studied for applications in fuel cells. The direct methanol-air fuel cell is usually operated in the presence of highly corrosive acid electrolytes in order to reject carbon dioxide. This requires the use of highly stable catalysts and supports as electrode materials. Pt is one of the few stable catalyst materials showing significant activity for methanol oxidation. Korzenuewski and Childers (1998) demonstrated that formaldehyde, which is often not detectable with any modern in situ analysis techniques, could be produced in significant amounts during electrochemical oxidation of methanol on Pt. Swathirajan and Mikhail (1992) prepared Pt-Sn catalysts on poly(3-methyl)thiophene and found that Pt-Sn catalysts were dispersed within the polymer at Pt loadings less than 60 $\mu g/cm^2$, but at higher Pt loadings, the platinum thin film also grew outside the polymer. Methanol oxidation was appreciable only at Pt loadings higher than 60

μg/cm^2, whereas hydrogen oxidation occurred at a Pt loading of 20 μg/cm^2. Haner and Ross (1991) studied the geometric and electronic effect of tin atoms in different chemical states on/in the platinum surface by using single-crystal faces of the ordered alloy Pt$_3$Sn and single-crystal faces of pure Pt modified by electrodeposited/adsorbed tin. They found that none of the alloy surfaces were more effective catalysts than any of the pure platinum surfaces under their conditions and that alloying platinum with tin to any extent significantly reduced the activity. They also proposed that a mechanism of catalysis is a hybrid homogeneous-heterogeneous sequence based on known homogeneous Pt-Sn catalysts.

However, the application of these catalysts to control the emission of methanol is inexpedient because they cannot achieve complete oxidation to CO_2 especially at low temperatures. The preparation of new catalytic systems for low temperature complete oxidation of methanol to CO_2 is a matter of continuous interest. The development of a catalytic method for purification of gases from methanol calls for a detailed study of the oxidation reaction mechanism and reaction kinetics.