CHAPTER I

INTRODUCTION

Very few products manufactured today are free from waste streams. Wastewater treatment was a prime consideration in the 1960s and 1970s in the United States, and today this has been met mostly with success in cleaning up many rivers and lakes. Probably more common, but many times less noticeable, is the emission of organic compounds from manufacturing the multitude of consumer products used every day. In most manufacturing processes, either for the raw materials, intermediates, or the finished products, organic materials are present as chemicals, solvents, release agents, coatings, decomposition products, pigments, and so on that eventually must be disposed. In such manufacturing, there are usually gaseous effluents that contain low concentrations of organics and are vented into the atmosphere. Examples of commercial operations that produce volatile organic compounds (VOCs) emissions are chemical plants, petroleum refineries, pharmaceutical plants, automobile manufactures, airplane manufactures, food processors, fiber manufactures, textile manufactures, printing plants, can coating plants, painting facilities etc. These organics present depend on the process and can include ketones, aldehydes, aromatics, parafins, olefins, acids, chlorinated hydrocarbons, and higher molecule weight organics, which often are present as aerosols. A number of methods are available for abating these emissions, including liquid absorbtion, solid adsorbtion, scrubbing, precipitation, condensation, membrane filtration, biodegradation, thermal incineration, catalytic incineration etc. Thermal incineration is the most effective way of ensuring complete destruction of VOCs and normally performs at temperatures in excess of 700 $^{\circ}$C. To lower the operational temperature and to make the process more economical, adding a catalyst, which is called catalytic incineration, can enhance the combustion process. The catalytic incineration method has become most popular because its operation temperature is low, in many cases, more versatile and economical for the low concentrations of organic emissions (i.e., < 5,000 vppm). Catalytic oxidation of VOCs in air is carried out at low reactant concentrations and with a very large stoichiometric excess of oxygen.

The basic catalytic oxidation reaction of an organic molecule is shown below:

$$HC + air (O_2) \xrightarrow{\text{catalyst}} CO_2 + H_2O \qquad (1.1)$$

The actual operating temperature and amount of preheat, depend on the organic molecule, space velocity, composition of feed (i.e., contaminants, water vapor, and so forth), and organic concentration.

One way of comparing thermal versus catalytic abatement is to look at the energy required (air preheat temperature) to obtain a particular quantitative removal of a given hydrocarbon species. The operating temperatures shown in Table 1.1 are well below the corresponding temperature necessary to initiate thermal (noncatalytic) oxidation. The catalyst initiates reaction at lower temperatures. This demonstrates the major advantage of catalyzed processes, which is that they proceed faster than noncatalytic reactions, allowing lower temperatures for the same amount of conversion. This translates directly into improved economics for fuel use and less expensive reactor construction materials, since corrosion is greatly reduced.

Heterogeneous catalytic oxidation is a well-studied and industrially useful process. Catalytic oxidation, both partial and complete, is an important process. By far, the majority of oxidation catalysts and catalytic oxidation processes have been developed for these industrially important partially oxidized products. However, there are important differences between the commercial processes and the complete catalytic oxidation of VOCs at trace concentration in air. For instance, in partial oxidation, complete oxidation to CO_2 and H_2O is an undesirable reaction occurring in parallel or in series to the one of interest. Other differences include the reactant concentration and temperature, the type of catalyst used, and the chemical nature of the oxidizable compound. Industrial catalytic oxidation reactions are carried out at high reactant concentrations over a variety of supported metal catalysts. Because most industrial processes operate with well-characterized inlet streams (usually one reactant plus an oxidant), there has been little need to understand the complex processes that may occur in mixtures. In contrast to these industrial reactions, catalytic oxidation of VOCs in air is carried out at lower concentrations (often less than 1,000 ppm) and with a very large stoichiometric excess of oxygen. Because

oxidation is a highly exothermic reaction, and because industrial reactions are generally carried out at high reactant concentrations, these processes are usually net producers of heat. When the reactant concentration is low, the processes are net consumers of heat if the entire gas stream must be heated to an elevated temperature. It may be expensive to heat the entire gas stream to a high temperature (e.g., >400 °C) to achieve a high reaction rate. As a result, catalytic oxidation of trace concentrations of VOCs is more economical if the reaction is carried out at lower temperature.

To do this, a highly active, nonselective catalyst is required. This is in direct contrast to almost all industrial oxidation reactions where selectivity for partial oxidized products is essential. Another consideration for removal of trace contaminants is that, if the oxidation is incomplete, compounds more toxic than the trace contaminant may be formed.

Selection of effectively catalytic materials for various organic pollutants has been the subject of many studies. For VOC oxidation, the applied catalysts can be divided into three main classes: supported noble metals, single or mixed metal oxides, and the combinations of noble metal and metal oxide. The active catalyst materials can be supported on thermostable substrates or even fabricated in the form of honeycombs. The precious metal catalysts are available in granular and monolithic forms or as foams and, the base metal oxide catalysts are mostly in granular form.

Metal oxide catalysts for oxidation processes normally consist of oxides of Group VB through IB of the period table. As a general rule, these catalysts are more poison-tolerant than supported noble metals, though they are also somewhat less active for oxidation reactions. The choice of catalytic components, support materials, and structural design (i.e. particulate or Honeycomb structures) is obviously dependent on the nature of the pollutants, potential poisons present in the gas stream, the degree of abatement required, the operating conditions, desired catalyst life, and ultimately economics. Catalytic oxidation systems are typically limited to streams containing low VOC concentrations.

Platinum oxidation catalysts, which have highly active and non-selective properties, and remain thermally stable until 650 °C, are the most commonly used

ones for air purification. Table 1.2 shows some Pt/Al_2O_3 catalysts developed for VOC oxidation applications.

Addition of a second metal component may give the catalyst higher stability. Coking is decreased, and the metallic crystallites appear more resistant to aging. Bimetallic catalysts are widely used but there is controversy as to the exact nature of interactions between the two metallic components, which leads to the positive bimetal effect. Often the extent of interaction between the metallic components in a dispersed state is correlated with the ease of alloy formation in the bulk state, though this may not always be true especially in the case of small particles dispersed on a high surface area support. It is essential to correlate the microstructure and surface composition of the catalyst with its adsorption behavior and reactivity. In order to successfully do that one has to be able to determine the nature of metal-metal and metal-support interactions that occur in the particular catalyst system that is being investigated. In bimetallic catalysts alloys may or may not be formed. If proof of significant alloy formation is present then it would be reasonable to assume that these alloys contribute to the bimetal effect. Even if alloys are not present there could be significant interaction between atoms of the primary metal and atoms of the secondary metal in supported bimetallic catalysts. It is important to understand the nature of this interaction as this could significantly alter the behavior of the catalyst. Additives such as Sn have proven to increase the long-term activity and performance of platinum catalysts for reforming applications in the oil industry. To the best of our knowledge, there have been no systematic studies of the effect of Sn additives in maintaining the activity of Pt VOC oxidation catalysts.

In this work we have studied two different series of $Pt-Sn/Al_2O_3$ catalysts. The first series was prepared by coimpregnation, while the second series was prepared by sequential impregnation with Sn first followed by Pt as second component. In both of the preparation methods, the primary metal (platinum) nominal loading was kept constant at 1 wt% while the amount of the second metal was varied. The adsorption behavior, surface composition, and the activity for methanol oxidation have been investigated. An effort has also been made to correlate the surface characteristics of the catalysts with their bulk composition and structure, which were determined using transmission electron microscopy, high-resolution

transmission electron microscopy, and energy disperse X-ray spectroscopy. The adsorption behaviors of the catalysts were studied by static-volumetric chemisorption and pulse chemisorption of hydrogen and oxygen. The surface oxidation states of the components of the catalysts were obtained by X-ray photoelectron spectroscopy. A flow reactor was used to study the oxidation of methanol.

Table 1.1 Operating temperatures for catalytic abatement of volatile organic compounds

Name of constituent	Chemical formula	Operating temperature ($^{\circ}$C)	Concentration before treatment (ppm)
Styrene	$C_6H_6CHCH_2$	250	310
Acetaldehyde	CH_3CHO	350	240
Benzene	C_6H_8	210	380
Toluene	$C_6H_5CH_3$	210	320
M-xylene	$C_6H_5(CH_3)$	210	270
Phenol	C_6H_5OH	300	380
Formaldehyde	HCHO	150	410
Acetic acid	CH_2COOH	350	590
Acetone	CH_3COCH_3	350	410
Ethyl acetate	$CH_3COOC_2H_5$	350	350
Methyl alcohol	CH_3OH	150	830
Ethyl alcohol	C_2H_5OH	350	550
Carbon monoxide	CO	150	4,000

Table 1.2 Examples of Pt/Al$_2$O$_3$ VOC oxidation catalyst applications

Gas stream composition	Gas stream temperature (°C)	Pressure (atm)	Space velocity (vol/hr)	Application
Diamine in air	230-300	1	NR	Odor removal from nylon production gases
Mineral oil and other vaporsw from an offset printing process	300-400	1	NR	Odor control from offset printing
374 ppm ethanol, 194 ppm n-propanol, 11 ppm n-propylacetate	260-370	1	30,000-70,000	Control of emissions from printing process
H$_2$, NO, CO, C$_3$H$_6$, CO$_2$, H$_2$O in 0.6-2.1% O$_2$, 83%N$_2$	200-500	NR	30,000	Exhaust control