

CHAPTER II

LITERATURE REVIEW

2.1 Background

The catalysts for catalytic oxidation of VOCs can be divided into three main classes: supported noble metals, single metal oxides and mixed metal oxide combinations (Spivey and Butt, 1992). Supported platinum is one of the most widely used catalysts for gases containing hydrocarbons and oxygenated hydrocarbons. However, platinum catalysts are susceptible to poisoning by chlorinated hydrocarbons. It has been known that bimetallic catalysts containing platinum and either palladium or rhodium can be applied in harsh reaction environments, such as automotive exhaust control, where the temperatures and space velocities tend to be very high. 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 knowledge, there have been no systematic studies of the effect of Sn additives in maintaining the activity of Pt catalysts.

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 choices of catalytic components, support materials, and structural design (i.e., particulate or Honeycombed structures) are 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.

Although there have been many previous Pt catalyst studies, the adsorption, desorption, and reaction of VOC molecules on Pt has not been widely investigated. Verbeek and Sachtler (1976) studied the adsorption and desorption of carbon monoxide, ethane, and deuterium on platinum, Pt₃Sn, PtSn, and PtSn₂. It was found that there were significant differences between the surface and the bulk composition of the alloys. From TPD experiments, it was revealed that as the proportion of tin in the alloys increased, desorption of the above-mentioned gases became progressively easier. This suggests a weakening of the chemisorptive bond caused by the adsorbing platinum atoms becoming surrounded by tin atoms (the “ligand effect”).

Gruber (1962) conducted experiments to investigate the adsorption of hydrogen, oxygen and carbon monoxide on platinum-on-alumina reforming catalysts and on the alumina base. The mechanism of CO adsorption on supported platinum was found to depend not only on the nature of the support but also on the degree of dispersion of the metal. Heat treatment of catalysts could decrease the dispersion of platinum. He also established a proposed mechanism for the oxidation-reduction cycle.

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 to 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°C. For all catalysts, reversible desorption of chemisorbed hydrogen occurred at approximately 175°C. It was suggested that the irreversibility of

the spillover hydrogen results from dehydroxylation of the support at a high temperature.

A TPD/TPR and reaction study of bimetallic Pt-Sn/Al₂O₃ catalysts by Sachdev and Schwank (1988) revealed that the average oxidation state of tin in the catalysts was Sn(II), without ruling out the possible presence of small amounts of zero valent tin and/or Pt-Sn alloys. The role of tin in the bimetallic catalysts was found to be very beneficial to maintain a high activity for n-hexane hydrogenolysis.

The catalysts used in this study have already been characterized by adsorption of H₂, O₂, and CO (Balakrishnan and Schwank, 1991). The particle sizes of the studied catalysts were determined by a transmission electron microscopy, and the platinum, tin, and chlorine contents were determined by a neutron activation analysis. An X-ray Photoelectron Spectroscopy (XPS) could provide information concerning surface compositions and oxidation states. The authors found that addition of tin on Pt resulted in significant differences in the gas uptake characteristics of three adsorbates. For both H₂ and CO, the experimental results indicated that an initial increase in gas uptake was obtained with addition of a small amount of tin. In the case of O₂ adsorption, there was a steady increase in gas uptake with increasing tin content. The XPS results of the reduced catalysts showed that most of the tin in alumina-supported samples was found in a valence state of either Sn(II) or Sn(IV). This finding indicates that interactions between the alumina support and tin prevent a complete reduction of tin.

The decomposition and oxidation of methanol on Al₂O₃, Pd/Al₂O₃ and PdO/Al₂O₃ 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 Al₂O₃ support which had been dehydrated and oxidized in 3% O₂ at 873 K for 10 min prior to TPD experiments. The main decomposition products of methanol were H₂ and CO which came off around 600-900 K with the maximum peak temperature at 780 K. On Pd/Al₂O₃, methanol decomposed

to form H₂ and CO between 400-700 K and had the maximum peak temperature of 500 K. The Pd surface area was 3.3 m²/g which is much less than the alumina surface area of 200 m²/g. This indicates 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 Al₂O₃.

Sen and Vannice (1988) found two types of adsorption configurations of acetone. The $\eta^1(\text{O})\text{-(CH}_3)_2\text{CO}$ state has been assigned to an acetone species bonding end-on via the lone pair electrons on the oxygen, and the $\eta^2(\text{O,C})\text{-(CH}_3)_2\text{CO}$ state was proposed to involve a species adsorbed with its C=O bond parallel to the surface sites, giving either π or di- σ bonding after rehybridization. These two types of adsorption configurations are quite different in reactivity. The more weakly bound η^1 species usually desorbs molecularly upon increasing the temperature of the surface, while the more strongly bound η^2 species desorbs at higher temperature, which can result in competitive decomposition and desorption.

Vannice et al. (1991) studied the desorption of acetone on clean Pt(111) surfaces using reflection-adsorption infrared spectroscopy (RAIRS) and high resolution electron energy loss spectroscopy (HREELS). They observed that the majority configuration is the η^1 structure. However, on the more open Pt(110) face or on step sites on a Pt(111) surface, η^2 di- σ bonding is preferred over η^1 on-top, which is mainly not due to an enhancement of the attractive interactions, but rather to a reduction of the steric-like repulsive interaction which was observed by Delbecq et al. (1993).

Liu and Vannice (1994) studied on the adsorption, desorption and decomposition of acetone on a Pt foil. It is known that the C=O bond in an acetone molecule is the strongest and hard to break. Therefore, C-H or C-C bonds in adsorbed acetone should be as close as possible to the surface. The $\eta^2(\text{O,C})\text{-(CH}_3)_2\text{CO}$ configuration favors this bond cleavage, in contrast to the experimental and theoretical findings on Pt(111) by Vannice et.al. (1991). It is conceivable that the defect site concentration on a Pt foil should be much higher than on nearly defect-free Pt(111) single crystal. These defect sites allow

stronger bonding of the η^2 species, which leads to side-on adsorption and decomposition to hydrogen at 364 K and carbon monoxide at 494 and 650 K.

There is, to the best of our knowledge, still no work reported about the adsorption, desorption and decomposition of ethylacetate on Pt catalysts. The closest work we could find deals with the chemisorption of formate and acetate on cluster models of Rh and bimetallic RhSn clusters (Papai et al., 1993).

2.2 Theory

2.2.1 Theory of TPD (Temperature-Programmed Desorption)

The simplest theoretical model describing gas-solid adsorption is the well-known Langmuir adsorption isotherm. This model will be recalled briefly in the case of both nondissociative and dissociative adsorption. The effect of kinetic parameters of the desorption phenomena has been qualitatively visualized by generating sets of theoretical TPD curves through a computer simulation (Delannay, 1984). The experimental variables, such as heating rate and carrier gas flow rate, also affect the desorption characteristics on a studied surface. Finally, the effect of diffusion limitations needs to be taken into consideration.

A. Nondissociative (First-Order) Adsorption

The adsorption process of a gas (G) on a solid (S) may be considered as a chemical reaction between a gaseous molecule or atom and some adsorption sites (S^*) present at the solid surface:



The Langmuir model is based on the hypotheses that a fixed number of sites N (F/cm^2) are present on the solid surface and that the enthalpy of adsorption (ΔH_a) is independent on the fraction of occupied adsorption sites. It is also assumed that both N and ΔH_a are temperature independent.

If N is the number of sites occupied at a given time (t) the rate of adsorption is given by

$$\frac{dN}{dt} = pkn_a(N^* - N) - k_dN$$

where:

N is the number of sites.

N^* is the number of occupied sites.

$N^* - N$ is the number of vacant sites.

p is adsorbate pressure over the solid.

kn_a is the kinetic constant of adsorption.

k_d is the kinetic constant of desorption.

In the case of a TPR investigation, the measured quantity is the adsorbate concentration (C) in the carrier gas sweeping the sample. In the case of an ideal reactor, it can be assumed that no axial or lateral concentration gradients exist. The TPD experiment is generally conducted by using a linear heating schedule. The following equations are obtained (Delannay, 1984):

$$C = -\frac{S}{F} \frac{dN}{dt}$$

$$C(T) = \frac{SN^* \theta A_d \exp(-E_d/RT)}{F + SN^* (1 - \theta) \sigma (RT / 2\pi M)^{1/2} A_o \exp(-E_o/RT)}$$

$$\frac{d\theta}{dT} = -\frac{F}{S\beta N^*} C(T)$$

where:

C is the adsorbate concentration in the gas phase (mol/cm^3).

S is the specific surface area of solid (cm^2/g).

F is the specific flow rate of the carrier gas ($\text{cm}^3 \text{ STP}/(\text{s}\cdot\text{g})$).

β is the heating rate (K/s).

σ is the surface area occupied by one adsorption sites (cm^2/mol).

θ is the surface coverage.

M is the molecular weight of the adsorbate (g/mol).

R is the universal gas constant ($J / (K \cdot \text{mol})$).

T is the absolute temperature (K).

A_d is the entropy factor.

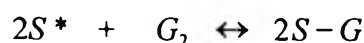
E_a is the activation energy of the adsorption process (J/mol).

A_a is the frequency factor.

E_d is the activation energy of the desorption process (J/mol).

B. Dissociative (Second-Order) Adsorption

Adsorption of gas molecules on a surface may lead to dissociation of the adsorbate into two or more fragments which then occupy surface sites. For desorption to take place, these fragments have to recombine. The dissociative adsorption of diatomic molecules such as H_2 , or O_2 may be viewed as a chemical reaction with surface sites.



The adsorption rate can be expressed by the following equation:

$$\frac{dN}{dt} = pkn_a(N^* - N)^2 - k_dN^2$$

The above equation is the second power with respect to the number of unoccupied surface sites (N^*-N) and occupied surface sites (N) as a consequence of the assumption that each dissociatively adsorbing molecule occupies two surface sites. The equations representing the TPD features can be described by the following relationships (Delannay, 1984):

$$C(T) = \frac{SN^* \theta^2 A_d \exp(-E_d/RT)}{F + SN^* (1-\theta)^2 \sigma (RT/2\pi M)^{1/2} A_a \exp(-E_a/RT)}$$

$$\frac{d\theta}{dT} = -\frac{F}{S\beta N^*} C(T)$$

C. Diffusion-Controlled Desorption

Currently, the diffusion of the adsorbate in the pores of the solid has not been considered. However, there are some instances, especially on supported catalysts, where slow diffusion in the pores might control the rate of adsorption. A generally mathematical model of diffusion in the pores of a catalyst is extremely difficult and will, therefore, not be presented here.

2.2.2 Theory of TPR (Temperature-Programmed Reaction)

Gas-solid reactions can be divided into the five following steps (Delannay, 1984):

1. Transport of the gaseous reactant toward the solid-gas interface (diffusion)
2. Adsorption of reactant on the solid surface
3. Interfacial processes
4. Desorption of the gaseous products from the solid surface
5. Transport of the products away from the solid-gas interface (diffusion).

Each of these steps may be the rate controlling step of the process. The sorption (steps 2 and 4) and diffusion steps (steps 1 and 5) have been discussed in the previous section. The present section will therefore be focused on step 3.

Extensive reviews of proposed mechanisms for interfacial processes of gas-solid systems have been published. In this section, the processes most relevant to catalysis studies will be considered. To illustrate the influence of kinetic and other experimental factors, Delannay (1984) has developed theoretical TPR curves from selected model mechanisms.

The TPD and TPR techniques can provide interesting results and help toward a better understanding of a studied system, provided that other information, gained from other techniques, is available, for instance, a priori knowledge of the chemical nature and of the state of dispersion of the reactive phase is of considerable help in limiting the choice among the possible reaction mechanisms.