

# CHAPTER I

## INTRODUCTION

Currently, ecological awareness is extensively appreciable. Air pollution is dramatically worldwide concerned as it affects to public health and the environment. In the rapid industrial development and the growth in urbanization coupled with the population increment, many activities such as energy consumption, resource usage and motorization have elevated explosively. Ambient air quality becomes a serious public health problem and global scale impact. As economic growth, the general public demands better environmental protection. Consequently, environmental controls are tightened. In some countries, their governments strengthen the regulation and implement abatement technology in order to meet the recommended health guidelines.

### 1.1 Statement of Problems

The problem of NO<sub>x</sub> pollution will be described by its type, emission sources, the influence on the environment and public health, and the removal approaches.

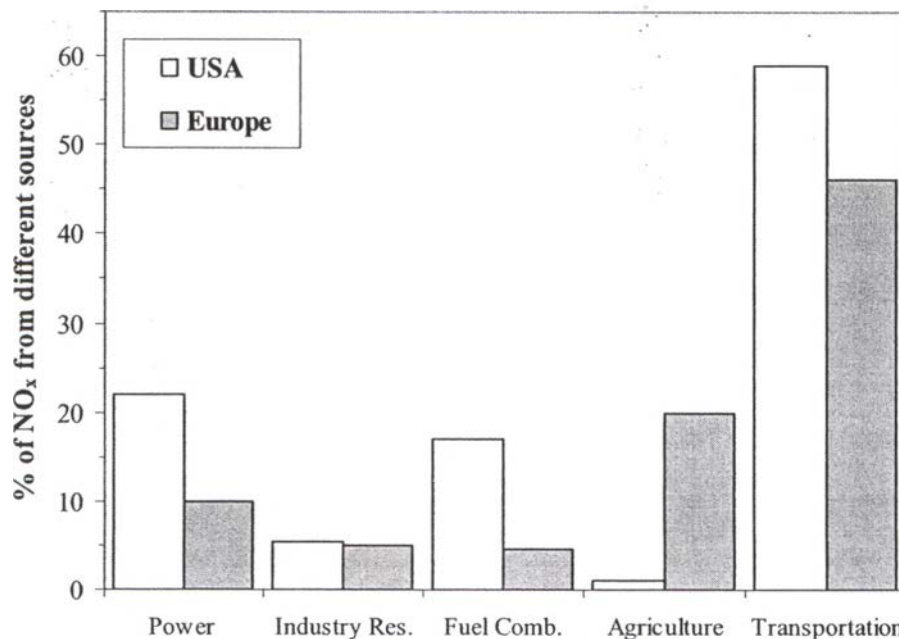
Nitrogen oxides (NO<sub>x</sub>) are a group of highly reactive gases which technically refer to nitric and nitrogen dioxide. It is recognized as one of the major principal air pollutants; for example, carbon monoxide, sulfur dioxide, and particulate matter. Generally, oxides of nitrogen are present in six gaseous forms (Peavy *et al.*, 1985): nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), nitrogen sesquioxide (N<sub>2</sub>O<sub>3</sub>), nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>), and nitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>). Among these components, only two forms of NO and NO<sub>2</sub> are primarily concerned in air pollution since they are released significantly to the atmosphere. Although NO is accountable for much larger proportion of the emission, most of the atmospheric burden is present in NO<sub>2</sub> form due to readily oxidation of NO by oxygen or ozone. In fact, nitrous oxide could not be ignored as it is a greenhouse gas and also involved in the stratospheric ozone degradation. It is known that this component is increasing at an appreciable rate.

### 1.1.1 Emission Sources of Nitrogen Oxides

The nature sources of nitrogen oxides include nitrogen fixation by lightening, volcanic activity and microbial activity. Nevertheless, the main emission source comes from the anthropogenic activities involving combustion processes. Figure 1.1 shows the distribution of the man-made emissions which can be classified into 2 main categories.

- 1) *Stationary source*: industrial process, energy production and waste incineration
- 2) *Mobile source*: gasoline and diesel engines

These sources emit nitrogen oxides mainly in forms of NO and NO<sub>2</sub>. Conversely, nitrous oxide is released relatively low by the natural microbiological processes so that it can be neglected. However, it is worth to note that N<sub>2</sub>O is produced mainly from non-selective oxidation process of ammonia in nitric acid plants (Janssen and Santen, 1999) and from adipic acid synthesis via cyclohexanone oxidation. In addition, there is considerable evidence that use of nitrogenous fertilizers increases the atmospheric level of nitrous oxide (Roy, 1997).



**Figure 1.1** Illustration of emission of NO<sub>x</sub> by source category in USA and European countries (Roy *et al.*, 2009).

### 1.1.2 Impacts of Nitrogen Oxides

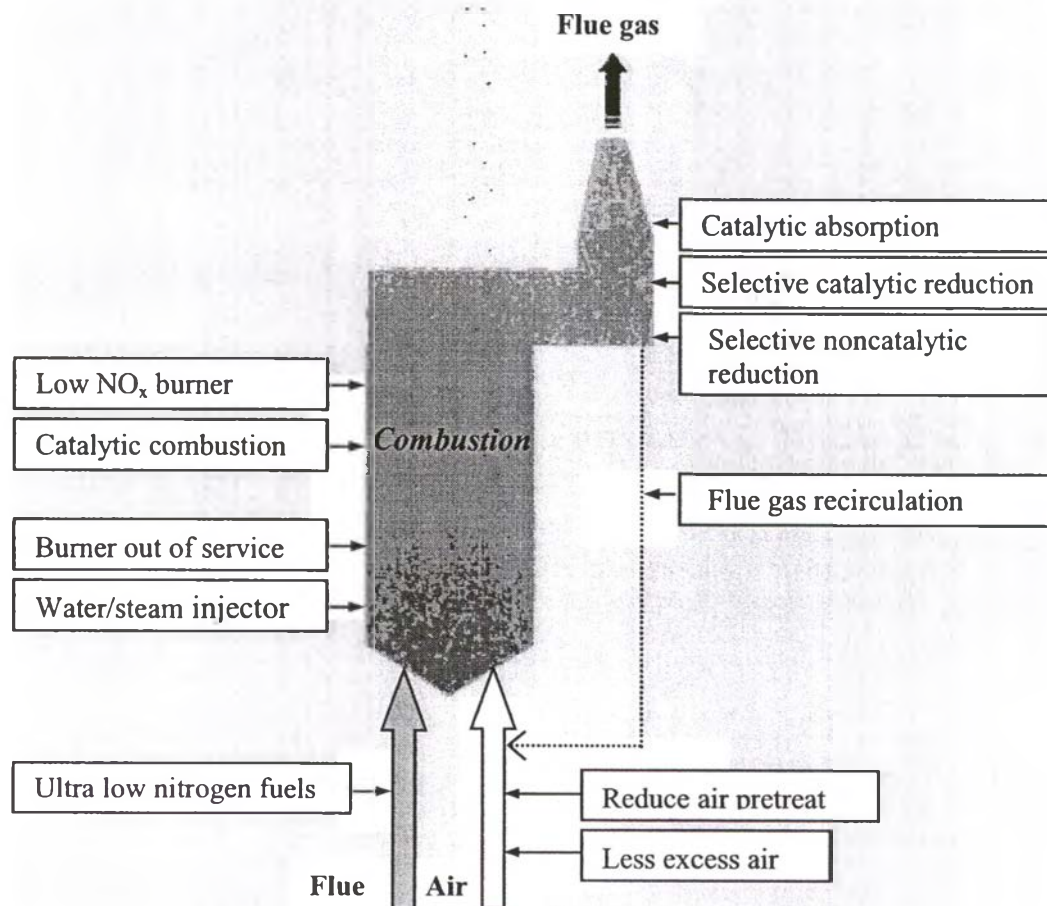
Nitrogen oxides have adverse effects to human health, ecosystems, agriculture and materials. Like carbon monoxide, nitrogen oxides can combine with the hemoglobin in the blood. Nitric oxide itself can destroy ozone through oxidation. As well as ozone, in the presence of air, NO is easily oxidized by O<sub>2</sub> forming NO<sub>2</sub>. This oxide poisons to the respiratory system and decrease in lung functions because it can diffuse through the tissue and damages the cell structure toward its oxidative reactivity (Fritz and Pitchon, 1997). This results in viral infection and immune system alteration. In addition, nitrogen oxides can produce secondary pollutants such as ground level ozone and peroxyacetyl nitrates (PAN) during their atmospheric reactions with reactive hydrocarbons under sunlight. These resulting compounds can trigger a serious respiratory problem and cause some damages to plants. Additionally, various photochemical compounds formed by these chain reactions are termed as photochemical smog. It also leads to visibility reduction.

Generally, the oxides of nitrogen retaining in the atmosphere may be transformed through the chemical process to nitric acid, acid aerosols, nitrates and nitrites as particle form; so called atmospheric aerosol. If the particulates are further washed out by precipitation, the dissolution of nitrates by an atmospheric water droplet will allow the additional formation of nitric acid. It contributes to acid rain which causes material damages, vegetation deterioration and acidification in both terrestrial and aquatic system. Ultimately, it disturbs the ecological system. Additionally, the small quantity released nitrous oxide is a potent greenhouse gas and destructive to ozone (Centi and Perathoner, 2007).

### 1.1.3 NO<sub>x</sub> Control Technologies

There are several techniques adopted for NO<sub>x</sub> emission control. These can be categorized into 3 groups: pre-combustion control, combustion control, and post-combustion control. Summary of these techniques is briefly illustrated in Figure 1.2. The first group is to lower the content of nitrogen compound originally presenting in the fuel through a hydrotreating process while the emission resulted from various fuels combustion such as natural gas, gas oils, and coals can be controlled by the latter group. It is the combustion modification which limits the

formation of  $\text{NO}_x$  during the actual combustion. This combustion control can be performed by various strategies such as reduce peak temperatures, control residence time and lower oxygen concentrations in the flame zone (Cooper and Alley, 2002). The last group is flue gas treatment technique. It removes nitrogen oxides from the exhaust gases after these compounds have been formed. This post-combustion control can be sub-divided into wet and dry systems. The wet methods or chemical scrubbing are chemical oxidation/absorption processes. This is normally applied to small  $\text{NO}_x$  emission sources. The dry methods include catalytic and non-catalytic process. Several techniques are classified in this group such as selective non-catalytic reduction (SNCR),  $\text{NO}_x$  decomposition, selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR),  $\text{NO}_x$  storage and reduction (NSR), adsorption and radiation.



**Figure 1.2** Possibilities for  $\text{NO}_x$  reduction from a combustion chamber (Grassian, 2005).

Among these  $\text{NO}_x$  controls, catalytic technologies are attractive because of their high efficiency with selective activity and economic balance. In principle, the simple NO decomposition is a thermodynamically favored reaction at low temperature (below 900 °C) and could be applied. However, the reaction is very slow due to high activation energy and highly efficient catalysts have not been discovered so far. Consequently, a reducing agent is necessary to convert NO into  $\text{N}_2$ . There are many alternative reducing agents currently proposed. Hydrocarbons such as propene are the promising substance to facilitate high selective reaction. Ammonia is also the important candidate to enhance the  $\text{N}_2$  selectivity. Recently, urea has been studied in the  $\text{NO}_x$  removal in diesel exhaust as an indirect source of ammonia because of its harmlessness. Moreover, there are many attempts to develop the material that possesses a wide activity window over operating temperature ranges and better performance under lean conditions. These are crucial factors in the automobile application.

## 1.2 Objectives

Improving fuel consumption in automobiles has become a significant factor in energy crisis and global warming from emission of carbon dioxide green house gas. To meet the global trend, the automotive industry aims to shift toward lean-burn operating engine which possesses the conditions that three-way catalysts could not serve for  $\text{NO}_x$  emission control. To find out a novel class of catalysts in the reduction of  $\text{NO}_x$  in oxygen rich conditions remains challenge.

Consequently, the main aim of this research is to develop highly active and selective catalysts that can convert  $\text{NO}_x$  to harmless product  $\text{N}_2$  under lean-burn conditions and try to understand mechanisms of the reaction. We have developed and investigated two main catalyst categories: Au and Pt supported on alumina. Sol-gel technique was proposed for catalyst preparation to obtain higher surface area and better performing catalyst. In this work, the sol-gel synthesis was sub-divided into two techniques according to the introducing procedure of an active metal into alumina. These were single step sol-gel and active metal doping on preformed sol-gel



alumina techniques. The performance of several catalysts synthesized from sol-gel and other preparation methods was carefully explored.

The activity of the catalysts was studied under various oxidative conditions. Different reducing agents such as hydrocarbons and urea were introduced to the reaction in order to promote the selectivity to  $N_2$ . As well as the catalytic activity, the stability of catalyst was studied under hazardous conditions by introducing  $SO_2$  and  $H_2O$  to the system. In order to understand the microstructure of catalysts and the mechanism of reaction, different characterization techniques were carried out as well.

### 1.3 Outline

This dissertation is organized into several chapters. It begins with introduction part and problem statement including the work objectives in this chapter. Brief background of nitrogen oxides gases, sol-gel chemistry, and the literature reviews of nitrogen oxides removal are given in the chapter II. Mechanism and the reactions related in selective catalytic reduction of nitrogen oxides are also described in this chapter. Chapter III will give the experimental information. It provides details of the materials used in the experiment and the apparatus set up. In addition, the principle and procedure of catalyst synthesis and instrumental analysis are explained accordingly.

The results and discussion are classified into three parts. Chapter IV will show  $NO_x$  selective catalytic reduction by urea which was introduced to the system in gas phase. The activities of different Au and Pt supported on alumina catalysts were investigated. In contrast, chapter V shows the performance of Pt catalysts under the same reducing agent, urea, but it was originally injected to the system as a liquid phase. Urea decomposition and its derivatives formation are discussed as well. Finally, chapter VI will illustrate the catalytic performance in terms of activity, selectivity and stability by propene coupled with the effect of sulfur and water. It also includes the comparison of various catalysts synthesized from several methods.

The summary and conclusions including recommendations for the future work are shown in the last chapter VII.