CHAPTER I

INTRODUCTION

The dramatic increase in public awareness and concern about the state of the global and local environments, which has occurred in recent decades, has been accompanied and partly prompted by an ever growing body of evidence on the extent to which pollution has caused severe environmental degradation. The introduction of harmful substances into the environmental has been shown to have many adverse effects on human health, agricultural productivity and natural ecosystems. Nevertheless, it is increasingly surprising just how resilient global environmental systems are to many of the pollutant burdens imposed upon them.

Although problems such as the destruction of valued environments, soil erosion and the extinction of species are very important for the future of mankind, it is pollution, which arouses the most interest. This is because people realize that pollution impacts on them directly through effects on their health, their food supply, the degradation of buildings and other items of cultural heritage, as well as having overt effects on forests, rivers, coastlines and ecosystem that they are familiar with. The costs of these effects in the depreciation of resources, lost productivity and in cleaning up or improving polluted environments are high and are increasingly occupying the attention of governments and politicians around the world, especially in technologically advanced countries. With increased legislation intended to reduce and prevent pollution, there is a corresponding increase in the involvement of specialist consultants, lawyers, insurers and financiers. There are many members of a wide range of professions with a growing interest in environmental pollution.

Attempt to alleviate environmental problems is relayed through the development of various technologies employed to be appropriate with each circumstance. Environmental catalysis is one effective solution that plays a major role in controlling the emission of environmentally unacceptable compounds. This technology also encompasses the application of catalysts for the production of alternative, less polluting products, waste minimization, and new routes to valuable products without the production of pollutants. Hence, within the chemical industry, there are two general strategies to address the environmental issue. They are developing technologies that either eliminate or minimize negative environmental impact, and secondary prevention. Examples of the first approach include new routes to MDI (methy-lenedi-isocyanate) that eliminate the need for phosgene and avoid the formation of HCl [1] or the commercialized production of 1,4-butanediol from butadiene that avoids the production of propargyl alcohol and the use of formaldehyde in Reppe process [1]. An example of the second approach is the use of selective catalytic reduction technology to remove nitrogen oxides from stationary source in combustion plants [2]. In fact, several chemical processes can not intrinsically avoid the formation of polluting substances; therefore, the second strategy has necessarily been useful in this situation.

Nitrogen oxides (NO_x) are important air pollutants, which are emitted unavoidably from both stationary and automotive sources and contribute largely to a variety of environmental problems such as the formation of acid rain and the resultant acidification of aquatic systems, the photochemical reaction in the stratosphere destroying the ozone in the atmosphere, and the harmful impact for the respiratory system of human being [3]. In general, focusing on the mechanisms of formation, three types of NO_x can be distinguished into thermal NO_x formed by the fixation of atmospheric nitrogen, fuel NO_x formed by the oxidation of the nitrogen-containing compounds in the fuel, and prompt NO_x formed by the oxidation of intermediate HCN [4]. Within NO_x, the existence of seven oxides of nitrogen is well known in form of NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4 and N_2O_5 [5]. However, of these seven oxides of nitrogen, nitric oxide (NO) and nitrogen dioxide (NO_2) are only the two most important air pollutants because they are emitted in large quantities, especially with NO representing 90 to 95% of the total NO_x [2]. The various chemical transformations of nitrogen oxides in the lower atmosphere are summarized in Figure 1.1. It is noted that nitric oxide is the key starting point for all of the other oxides of nitrogen. It is not only produced by the burning of fossil fuels, but also by lightning, microbial decomposition of proteins in the soil, and volcanic activity. Once produced, nitric oxide is rapidly oxidized by ozone, OH, or HO_2 radicals to form the higher oxides of nitrogen such as NO_2, HNO_2, and HO_2NO_2 [6]. Thus, if nitric oxide is prevented from entering the atmosphere, most of the downstream effects of NO_x pollution can be eliminated.

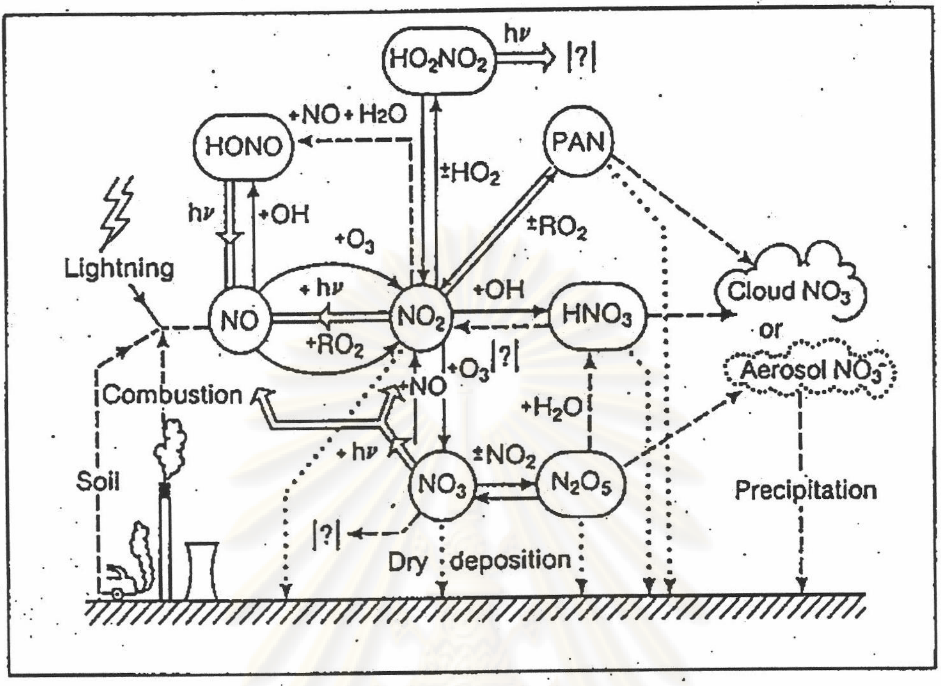

Figure 1.1 Chemical transformations of atmospheric NO_x: (═══>) photochemical process, (———>) thermal gas-phase processes, (·········>) dry deposition, and (– – – ->) heterogeneous reactions [2]

To remove NO_x, there are a number of commercial approaches including adsorptive, thermal and catalytic methods [6]. Basically, the major disadvantages of two formers are the loss of costs to eliminate the remaining NO_x on adsorbent in adsorptive processes and the loss of energy consumption in thermal processes. Hence, the catalytic technologies have been much promising in the present time. Typically, there are two major conventional catalytic procedures for the abatement of NO_x emissions into the atmosphere. Both represent remarkable achievements of chemical technology that contributes to the sustainability of global and local environments. The first technology is the selective catalytic reduction using ammonia as a reductant (NH_3-SCR) discovered in 1957 [7]. It is a process in which ammonia reacts selectively with NO_x to produce N_2 without consumption of the excess oxygen. However, there are many problems associated with this process including ammonia slip, equipment corrosion, as well as danger in transportation and storage of ammonia [8]. Hence, this technology can be conveniently used for only stationary sources such as oil-fired power plants. The second technology is the three-way catalyst (TWC) that is highly efficient in the simultaneous removal of carbon monoxide, hydrocarbons and nitrogen oxides [9]. However, it requires an exhaust gas composition operating very close to the stoichiometric point, which is restrictedly found in gasoline-fueled automobiles. The emissions from diesel and lean-burn gasoline engines are not satisfactorily controlled on this catalyst due to a dramatic decrease of NO_x conversion under the strongly oxidizing atmosphere. Thus, the serious problem for NO_x removal in practice is that neither of the above two conventional catalytic technologies is applicable for the emissions from both stationary and mobile sources containing a large excess of oxygen. Hence, a new catalytic technology is extremely required for the abatement of dilute NO_x in these emissions.

The initiative to reduce NO_x under lean-burn conditions was conceived from the discovery of the catalytic decomposition of NO to N_2 over a Cu-exchanged zeolite catalyst in the early 1980s [10]. This method is feasible because no reducing agent is required. Thermodynamically, NO can decompose to N_2 under 800°C but, kinetically, it remains stable in the absence of catalyst [11]. Unfortunately, the most promising systems for NO decomposition, such as Cu-based zeolites, do not suppress the inhibiting effect of oxygen, which remains the single most important obstacle to overcome in the development of a successful $DeNO_x$ catalyst [12]. Hence, it has been clear that this reaction of NO decomposition can not be contemplated for a real technological application in the presence of a complex exhaust mixture, although it has and will continue to be a subject of research interest [13].

Due to the lack of success in developing feasible NO decomposition catalysts, the alternative approach of the selective catalytic reduction of NO to N_2 using diesel-fuel-derived hydrocarbons is under intensive investigation by engine manufacturers, catalyst companies and universities throughout the world. In 1986, the outstanding activity for the catalytic decomposition of NO on Cu-ZSM-5 compared to the earlier known catalysts was reported [14]. This finding was remarkable but its catalytic activity dropped sharply with a decrease in the NO concentration and this catalyst suffered from severe deactivation in the presence of oxygen, sulfur oxides or water vapor. It was later demonstrated that Cu-ZSM-5 showed a significant activity when it was used for a real lean-burn engine; moreover, the rate of reaction increased in the presence of oxygen [15, 16]. It was shown that the reaction taking place in this case was not the decomposition of NO but the reduction of NO by hydrocarbons contained in the emission gases. In 1990, the two research works were independently reported that the reduction of NO over Cu-ZSM-5 could be greatly enhanced in an excess of oxygen by the presence of small amounts of hydrocarbon [17, 18]. Following this discovery, a number of catalysts such as various kinds of solid acids and bases, including ZSM-5 loaded with metal ions, have been demonstrated to be active catalysts for this reaction. Generally, this reaction is the so-called selective catalytic reduction by hydrocarbon (HC-SCR).

Since the 1990s, although numerous materials, such as ion-exchanged zeolites [19-43], metallosilicates [44-48], single metal oxides [49-58], mixed oxides [59-63], perovskites [64-68], supported transition metals [69-83] and supported noble metals [84-98], have extensively been studies, the promising catalysts seem to be ion-exchanged zeolites as much. Cu-ZSM-5 is one of the most active zeolite-type materials currently known for reduction of NO by hydrocarbon in oxidizing environments [19-28]. Indeed, it is very active for the selective catalytic reduction of NO with light hydrocarbons at temperature above 350°C; however, the maximum NO conversions are only 40-50% in the actual auto exhaust due to inhibition and poisoning by water vapor and sulfur dioxide [99-101]; moreover, Cu-ZSM-5 sinters readily under typical high temperature exhaust conditions [102-104]. Technical performance requirements for automotive lean-burn catalysts depend on the particular engine for which they are to be used. The duty cycle for an engine determines the exhaust temperature, gaseous flow rate and exhaust composition. However, in most diesel-fueled vehicles, the catalysts must resist deactivation after exposure to temperatures up to about 700°C. Hence, new catalyst formulations based on modifications to Cu-ZSM-5 having higher SCR activity and thermal stability have been reported [105-109]. Nevertheless, the hottest regions of diesel exhaust operation exceeding 700°C still present a major problem for these and other zeolites, which typically deactivate above 700°C, especially in the presence of water vapor. Deactivation occurs primarily by dealumination, which results in the Al migrating out of the zeolite framework structure thereby causing a loss in the catalytically active Cu ions bound to the Al sites [110]. Evidence for this mechanism has been confirmed using ^{27}Al NMR, which shows a decrease of over 50% in the number of Al ions occupying tetrahedral sites in the zeolite framework after aging [111]. Another serious disadvantage of Cu-ZSM-5 catalyst is their vulnerability to deactivation due to poisoning by sulfur oxides. Since sulfur is ubiquitous in both diesel fuel and engine oil, improvements in sulfur tolerance must be made. However, it may be possible to improve its poison resistance and thermal stability.

Based on presently available evidence about the disadvantages of Cu-ZSM-5 catalyst, the two alternative ways to improve the catalytic performance are the stabilization of the structure of zeolite-type catalysts upon hydrothermal deactivation and the development of non-zeolitic systems being much resistant to various inhibitors and having high stability in real conditions. On the second way, Pt-based catalysts have received much interest for lean NO reduction using on-board hydrocarbons, since they retain their activity for NO reduction after high temperature laboratory and diesel engine aging [112]. Furthermore, they are generally resistant to sulfur dioxide poisoning [113]. In General, the catalyst formulations containing Pt are the most active for NO reduction with hydrocarbons between 200 and 300°C, whereas Cu-ZSM-5 formulations catalyze reduction of NO with hydrocarbons above about 350°C as shown in Figure 1.2. Data in Figure 1.2 show that the conversion for Pt reaches a maximum at about 250°C according to reaction 1.1, but then quickly drops to zero when the hydrocarbon reaction with O_2 following to reaction 1.2 becomes dominant and consumes the remaining hydrocarbon.

$$2C_3H_6 + 4NO + 7O_2 \rightarrow 2N_2 + 6CO_2 + 6H_2O \tag{1.1}$$

$$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O \tag{1.2}$$

The remarkable disadvantages for Pt-based catalysts become that they are not adequate for the very demanding challenge of providing high activity and good selectivity at high temperature range [114]. In addition, the high rates of N_2O formation [115-117] and the narrow temperature window of the catalytic activity [118-120] are also crucial problems for application in practice. Thus, the following major improvements will be needed for their successful, economic application: (1) a broadening of the NO reduction temperature window of operation, (2) an increase of the selectivity for NO reduction relative to hydrocarbon combustion, and (3) a decrease for the production of N_2O. However, the effective development and design of Pt-based catalyst remain important to understand intrinsically the reaction mechanism in order to give a judicious decision.

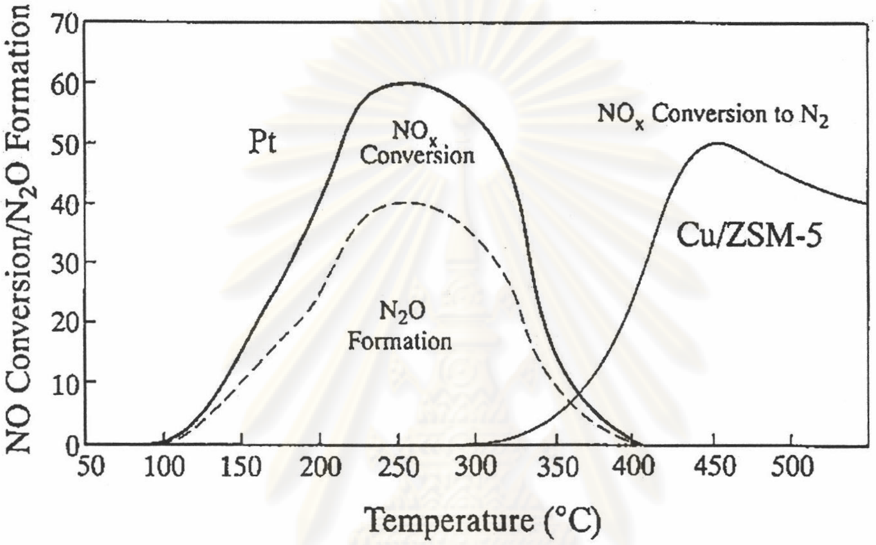

Figure 1.2 NO conversion and N_2O formation on Pt and Cu-ZSM-5 catalysts during the selective catalytic reduction with C_3H_6 under lean-burn condition [114]

At the present time, although there are many literatures reported to the success for testing the selective catalytic reduction of NO by hydrocarbons under excess oxygen over Pt-based catalysts, the outstanding knowledge about the reaction mechanisms and the active intermediate species is still ambiguous. The reaction mechanisms over Pt-based catalysts have been vastly proposed by employing various characterization techniques such as *in situ* Fourier transform infrared (FT-IR) spectroscopy [121-127], temporal analysis of products (TAP) [116, 128-130] and steady-state isotopic transient kinetic analysis (SSITKA) [131]. Generally, two main different mechanisms have been reported in the open literatures, i.e., the NO decomposition mechanism [116, 124, 125, 130-132] and the NO reduction mechanism [121-123, 126-129]. The NO decomposition mechanism mentions briefly that the hydrocarbons are contributed to remove the surface oxygen poisoning the active sites, while nitrogen product is dominantly formed via NO dissociation [116]. Hence, the complex surface species such as organic nitro species are distinctly neglected and either N atom or NO molecule is addressed as the intermediate species in this mechanism [133, 134]. On the other hand, the NO reduction mechanism is pronounced that the significant concept is the complex surface species playing an important role to produce nitrogen, although its pathway may be different in detail. Examples of this mechanism are that the hydrocarbons react with oxygen to partially oxidized hydrocarbons, which are subsequently reactive with nitrogen dioxide to form nitrogen [118, 135] and that the hydrocarbons may first react with nitrogen dioxide produced by NO oxidation to organic nitro species leading to the formation of nitrogen [123]. Thus, there are many types of surface species, e.g., oxygenated organic complex [122], organic nitro compounds [123] and isocyanate species [126], independently assigned as the intermediate species for this mechanism.

With the above-mentioned introduction, the previous mechanistic studies in the selective catalytic reduction of NO by hydrocarbon on Pt-based catalyst under lean-burn condition have not been clarified to take place through whether the NO decomposition or the NO reduction mechanisms. Consequently, an exact role of the catalytic surface species has not particularly been addressed as whether the intermediate species or the spectator species upon such reaction. Therefore, the objective of this work is the mechanistic studies in the selective catalytic reduction of NO with hydrocarbon under excess oxygen on a Pt/Al_2O_3 catalyst through the investigation of surface species. Typically, the previous conventional characterization of surface species reported in the open literatures has been made by using *in situ* Fourier transform infrared spectroscopy technique [121-127]. However, this procedure indeed indicates only one side of image about the nature of surface species and, perhaps, some insight can not be clearly identified. Hence, the other characterizations are necessary to accompany with it. In this research, the temperature programmed technique that is a basic method in the catalysis field is mainly useful for the investigation of surface species in a new aspect. Examples of the characterization include the observation of nature of surface species using an experimental set of three continuous steps consisting of reaction step, temperature programmed desorption step as well as temperature programmed oxidation step and the reactivity test of surface species to various oxidizing gases using temperature programmed oxidation technique. However, the influencing parameters, especially types of reductant, may be carefully taken into account for considering in detail about the reaction mechanism because the use of different reductant leads to the change of reaction mechanism [133, 134, 136-138]. At the beginning, C_3H_6 is selected as a model reductant due to its simplicity in chemical structure. In addition, the production of plenty of surface species with C_3H_6 and the proof that the overall reaction mechanism occurs on the only Pt surface [123-125, 134] result in the distinct investigation.

In order to understand better the proposed reaction mechanism, the additional experiments by the introduction of the second metal on a Pt/Al_2O_3 catalyst to disturb the function of active sites are also proceeded. The original idea for this testing is conceived from the discovery in the open literature that the main reaction mechanism in the selective catalytic reduction of NO by C_3H_6 is similar after adding any second metal (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo, Ti, Ag, Au, Pd, Rh) on a Pt/Al_2O_3 catalyst, although each second metal can have a significant influence (either positive or negative) on the catalytic activity [139]. Hence, it is speculated that the apparent differences in the catalytic activity of modified Pt/Al_2O_3 catalysts may assist in the identification of the intermediate surface species.

Following the above motivation, the scopes of this study have to be taken into account.

1. Prepare and characterize Pt/Al_2O_3 and $Pt\text{-}M/Al_2O_3$ (M = Li, Cr, Fe, Ni, Ga, Co, Sn and W) in order to use for the investigation of surface species.
2. Study the catalytic behavior in the selective catalytic reduction of NO by C_3H_6 under excess oxygen over a Pt/Al_2O_3 catalyst towards temperature programmed reaction in order to determine the temperature range for the production of the surface species.
3. Investigate the surface species produced on a Pt/Al_2O_3 catalyst in the selective catalytic reduction of NO with C_3H_6 under excess oxygen by emphasizing the temperature programmed techniques as follows:

- Study the nature of surface species by an experimental set of three continuous steps including reaction step, temperature programmed desorption step and temperature programmed oxidation step.
- Study the reactivity of surface species to various oxidizing gases by temperature programmed oxidation technique.
- Study the change of nature of surface species by adding the second metal (Li, Cr, Fe, Ni, Ga, Co, Sn or W) on a Pt/Al_2O_3 catalyst to disturb the function of active sites.

4. Predict the reaction mechanism of the selective catalytic reduction of NO by C_3H_6 under excess oxygen over a Pt/Al_2O_3 catalyst.
5. Apply the investigation of surface species with the reaction that gives the complicated mechanism, e.g., the selective catalytic reduction of NO under excess oxygen over a Pt/Al_2O_3 catalyst using C_3H_8 as a reductant instead of C_3H_6.

The present research work is divided into six chapters. The backgrounds of NO_x emission control and the motivation to study this topic are briefly mentioned in chapter I. Chapter II is concerned with literature reviews of the selective catalytic reduction of NO by hydrocarbons over platinum group metal catalysts under lean-burn conditions. Subsequently, a detailed overview of mechanistic studies in such reaction is compiled in chapter III. The experimental detail for the mechanistic studies in chapter IV consists of the catalyst preparation, the catalyst characterization and the catalyst evaluation. Next, chapter V demonstrates the experimental results including an expanded discussion. In the last chapter, the overall conclusions obtained from this work and some recommendation for any future works are present. Finally, specification of alumina support, calibration curves, various examples of calculation and list of publications, which have emerged from this study, are included in appendices at the end of this dissertation.