THE SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE BY PROPYLENE OVER BIMETALLIC CeO_2-ZrO_2 SUPPORTED CATALYST

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To my beloved parents
For your patience and understanding.

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ABSTRACT

Air pollution by nitrogen oxides (NO_x) is currently one of the most serious environmental problems. The conventional three-way catalyst shows low NO_x conversion in lean burn exhaust that contains high concentration of O_2. The selective catalytic reduction of NO (SCR-NO) with C_3H_6 in the presence of excess O_2 over bimetallic Cu-Ag catalysts supported on CeO_2-ZrO_2 was investigated in this study. Initially, it was found that the loading of Ag strongly promoted the catalytic performance of Cu(4)/CeO_2 catalyst, reaching a maximum NO conversion with the doping of 1 wt% Ag. The UV-Vis DRS results revealed that the major species on Cu(4)/Ag(1)/CeO_2 catalyst were isolated Cu^{2+} species and $Ag_n^{\delta+}$ clusters which are responsible toward a higher NO reduction activity. However, Cu(4)/Ag(1)/CeO_2 catalyst is not a promising catalyst for practical use due to its low activity in the temperature region of 250-350ºC. Extended studies were conducted to investigate the influence of different supports on the activity of SCR-NO. Cu(4)/Ag(1)/CeO_2(75)-ZrO_2(25) catalyst was observed to demonstrate higher NO conversions at low temperature region than the Cu(4)/Ag(1)/CeO_2 catalyst due to its strong metal-support interaction and high reducibility. It is presumed that these features would enhance the activation of C_3H_6 to selectively react with NO at low temperature region. Central composite design coupled with response surface methodology was employed to study the effect of operating variables on the SCR activity of Cu(4)/Ag(1)/CeO_2(75)-ZrO_2(25) catalyst and to determine the optimum NO conversion. The ranges of the temperature, NO concentration and C_3H_6 concentration used in this study were 224-576ºC, 818-2582 ppm and 818-2582 ppm , respectively as determined by the central composite design. The optimum NO conversion of 82.89% was obtained at 415.38ºC, 1827.16 ppm of NO concentration and 1908.13 ppm of C_3H_6 concentration. A Langmuir-Hinshelwood kinetic model was proposed for this study over Cu(4)/Ag(1)/CeO_2(75)-ZrO_2(25) catalyst. Prediction from the model agreed well with the experimental results. The model indicated that the surface reaction between adsorbed NO_x species and partially oxidized hydrocarbon was the rate-limiting step for this process.

ABSTRAK

Pencemaran udara oleh gas NO_x merupakan salah satu masalah alam sekitar yang paling serius dewasa ini. Mangkin tiga hala yang lazim digunakan menunjukkan penukaran NO_x yang rendah dalam enjin yang beroperasi dalam keadaan O_2 berlebihan. Dengan itu, pengurangan NO secara memilih dengan C_3H_6 bermangkinkan CeO_2-ZrO_2 yang diubahsuai dengan dua logam (Cu dan Ag) secara serentak telah dijalankan dalam kehadiran O_2 yang berlebihan dalam penyelidikan ini. Pada mulanya, penambahan Ag dalam mangkin Cu/CeO_2 didapati sangat menggalakkan aktivitinya dengan mencapai pengurangan NO_x maksimum dengan muatan Ag 1%. Keputusan UV-Vis DRS menunjukkan bahawa spesies Cu^{2+} terpencil dan gugusan $Ag_n^{\delta+}$ merupakan spesies utama dalam mangkin Cu(4)/Ag(1)/CeO_2 yang bertanggungjawab terhadap aktiviti pengurangan NO yang lebih tinggi. Namun demikian, mangkin Cu(4)/Ag(1)/CeO_2 bukan satu mangkin yang baik untuk digunakan secara praktikal disebabkan aktivitinya yang rendah dalam julat suhu 250-350ºC. Penyelidikan lanjutan telah dijalankan untuk mengkaji pengaruh penyokong yang berbeza terhadap prestasi mangkin. Mangkin Cu(4)/Ag(1)/CeO_2(75)-ZrO_2(25) menunjukkan prestasi pengurangan NO yang lebih tinggi daripada mangkin Cu(4)/Ag(1)/CeO_2 dalam julat suhu 250-350ºC disebabkan interaksi logam-penyokongnya yang kuat dan kadar penurunannya yang tinggi. Sifat-sifat ini dianggap akan menggalakkan pengaktifan C_3H_6 untuk bertindak balas dengan NO secara memilih dalam julat suhu 250-350ºC. Rekabentuk "central composite design" berganding dengan "response surface methodology" telah digunakan untuk mengkaji kesan pembolehubah proses terhadap prestasi mangkin Cu(4)/Ag(1)/CeO_2(75)-ZrO_2(25) dan menentukan nilai optimum penukaran NO. Julat suhu, kepekatan NO dan kepekatan C_3H_6 yang digunakan dalam kajian ini adalah ditentukan oleh rekabentuk "central composite design" iaitu 224-576 ºC, 818-2582 ppm NO dan 818-2582 ppm C_3H_6 Nilai optimum penukaran NO sebanyak 82.89% boleh dicapai pada 415.38ºC, 1827.16 ppm kepekatan NO dan 1908.13 ppm kepekatan C_3H_6. Satu model kinetik "Langmuir-Hinshelwood" telah diterbitkan untuk penyelidikan ini. Anggaran yang diperolehi dari model tersebut selaras dengan keputusan eksperimen. Model tersebut menunjukkan tindak balas permukaan antara spesies NO_x terjerap dan hidrokarbon teroksida separa merupakan langkah menghad kadar proses ini.

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a - Weight percent of CeO_2

A_m - Cross sectional area of adsorbate molecule

A/F - Air to fuel ratio

b - Weight percent of ZrO_2

B - Number of factorial runs

c - Constant, exponentially related to the heat of adsorption and the heat of liquification of the first layer

C_i - Concentration of species i

$C_{i.s}$ - Surface concentration of sites occupied by species i

C_t - Total concentration of sites on the catalyst

C_v - Molar concentration of vacant sites on the catalyst

CH - C_3H_6

$C_xH_yO_z$ - Carbonaceous deposit

CHO - Partially oxidized hydrocarbon

d - Planes spacing

D_β - Mean crystallite sizes

e - Reaction order for NO

E_A - Apparent activation energy

f - Reaction order for C_3H_6

F - Total reactant flow rate

F_{AO} - Inlet molar flow rate of NO/C_3H_6

$F_{SKM}(R_\infty)$ - SKM remission function

F/W - Ratio of the total reactants flow rate to the weight of catalyst

g - Reaction order for O_2

$\Delta G°$ - Standard Gibbs energy change of reaction at 25ºC and 1 atm

HC - Hydrocarbons

i - Number of data

k - Number of independent variables

K - Particle shape factor

k_a - Apparent rate constant

$k\mathrm{i}$ - Absorption rate constant of ith reaction

ks - Surface rate constant of the overall reaction

K_i - Equilibrium adsorption rate constant of i^{th} reaction

K - Absorption coefficient

n - Integer

$\mathrm{N_A}$ - Avogadro’s number

$\mathrm{n_0}$ - Number of repetition of the experiments at the center point

$\mathrm{NO_{initial}}$ - Concentration of NO in the feed

$\mathrm{NO_{final}}$ - Concentration of NO in the exit stream

P - Pressure

P_i - Partial pressure of species i

$\mathrm{P_0}$ - Saturation pressure

r - Rate of reaction

r_NO exp - Rate of NO reduction gained from experimental results

r_NO calc - Rate of NO reduction gained from kinetic model

R_∞ - Diffuse reflectance of the sample

R^2 - Determinant coefficient

S - Scattering coefficient

S - Vacant site

S_i - Selectivity of i^{th} product (%)

$\mathrm{S_{BET}}$ - BET surface area

$\mathrm{S_{SCR\text{-}HC}}$ - Competitiveness factor (%)

$\mathrm{T_{max}}$ - Maximum temperature

V - Total amount of gas absorbed at pressure P

$\mathrm{V_m}$ - Volume of gas absorbed at a monolayer coverage

W - Weight of catalyst

$\mathrm{W/F}$ - Ratio of the weight of catalyst to the total reactants flow rate or it is also known as time factor

x - Coded level of the independent variable

x - Weight percent of Cu

X - NO/C_3H_6 conversion

y - Response variable

y - Weight percent of Ag

θ - Diffraction angle

α - Star point

β - Full-width at half maximum height in radian

β - Regression coefficients

λ - Wavelength of X-ray

Σ - Summation of data

LIST OF ABBREVIATIONS

ALPO - Aluminophosphate
ANOVA - Analysis of variance
BET - Brunauer-Emmett-Teller's surface area model
CAAA - Clean Air Act Amendments
CCD - Central composite design
CIDI - Compression ignition direct injection
DOE - Design of experiments
DRS - Diffuse Reflectance Spectroscopy
EPA - Environmental Protection Agency
GAO - General Accounting Office
GC - Gas chromatography
GHSV - Gas hourly space velocity
I.D. - Internal diameter
M - Metal
MO - Metal oxide
NA - Nitrogen adsorption
NAAQS - National Ambient Air Quality Standard
NSR NO_x storage-reduction
OSC - Oxygen storage capacity
PAN - Peroxyacetyl nitrate
PI - Pressure indicator
ppm - Part per million
RSM - Response surface methodology
SAPO - Silicoaluminophosphate
SCR - Selective catalytic reduction
SCR-HC - Selective catalytic reduction of NO_x with hydrocarbons

SCR-NH_3 - Selective catalytic reduction of NO_x with NH_3
SKM - Schuster-Kubelka-Munk
SNCR - Selective non-catalytic reduction
S.S - Sum of square
STP - Standard temperature and pressure
TCD - Thermal conductivity detector
TPD - Temperature programmed desorption
TPR - Temperature programmed reduction
TWC - Three-way catalytic converter
USY - Ultra stable Y zeolite
XRD - X-ray diffraction
ZSM-5 - Zeolite Socony Mobil – 5

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Since their first appearance on the market, mankind has enthusiastically embraced the automobile. The enthusiastic public acceptance was predictable as motorized vehicles offer virtually unlimited flexibility, freedom and mobility. Although only within the reach of the fortunate and the wealthy few at first, they have now forced their way into modern society. It is hardly uncommon nowadays for a household to own two or even more cars or motorcycles.

Nevertheless, the environment that we depend on so much is paying a big price for the luxury of personal transportation. Acid rain and air pollution are very important problems that must be solved soon because such pollution has major effects on terrestrial and aquatic ecosystems. At present, one of the most significant problems is removal of NO_x, which are produced during high-temperature combustion and are an important group of air contaminants (EPA, 1998; and EPA, 2002).

Due to its explosive growth, automobile use has become one of the most important sources of environmental pollution today. Hence, the control of NO_x emissions for all vehicles are very essential, since 20-70% of NO_x generated from anthropogenic activities is attributed to the mobile sources (Lox and Engler, 1999).

The only counterweight to increasing vehicle use is increasingly stringent legislation with respect to emission limits. Subsequent legal norms are becoming tighter and tighter. The Clean Air Act of 1963 and its subsequent amendments set federal emissions control standards for all new cars and light trucks sold in the United States (GAO, 2000). The most recent Clean Air Act Amendments (CAAA) in 1990 established more restrictive "Tier 1" emissions standards, which became effective in 1994. The CAAA also required Environmental Protection Agency (EPA) to study whether more stringent "Tier 2" standards was needed to meet the National Ambient Air Quality Standards (NAAQS). In 1999, EPA determined that new standards were needed and cost-effective (EPA, 2002). Starting in 2004, all classes of passenger vehicles, including sport utility vehicles and light trucks, will have to comply with new average tailpipe standards of 0.07 grams per mile for nitrogen oxides as shown in Figure 1.1.

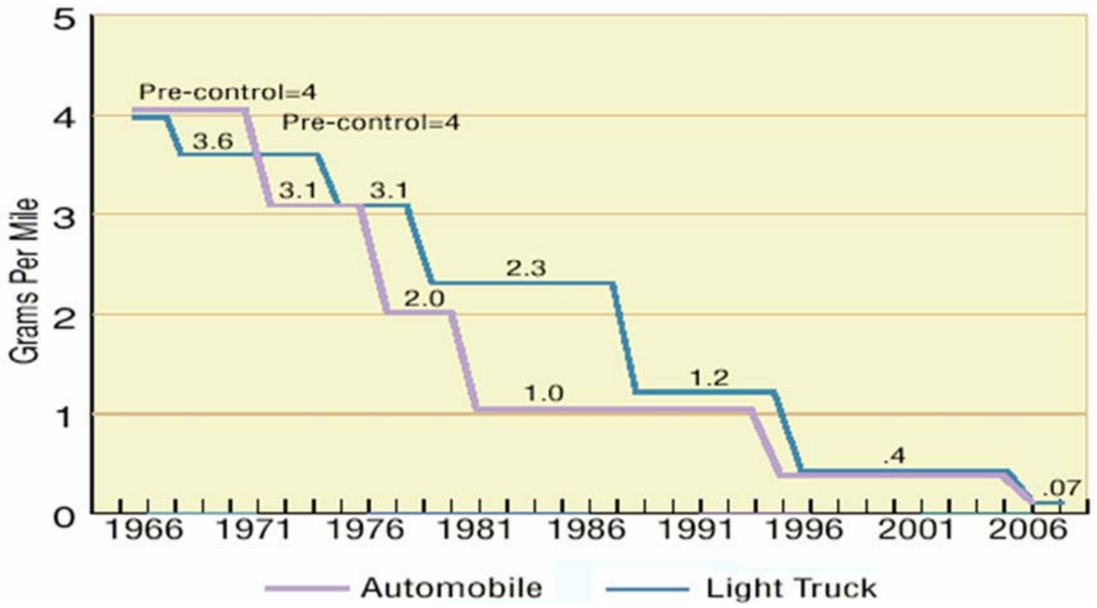

Figure 1.1 Standard of nitrogen oxide emission (Davis, 2000)

The three-way catalytic converter technology is the principal method of controlling the emissions from internal combustion engines from vehicles. This catalytic treatment has been in use since year 1979. The three-way catalytic converters used in automobile exhaust gas are produced from expensive noble metals (Pt, Rh and Pd). The TWC is capable to diminish the emission of hydrocarbons, NO_x and CO from gasoline-fuelled engines operate around the stoichiometric air to fuel ratio. However, three-way catalysts only achieve good simultaneous conversion of the main pollutants (CO, NO_x and hydrocarbons) in a relatively narrow window of the air-to-fuel ratio, which in turn can oscillate even in the presence of electronic control (Taylor, 1993).

As the concerns about global warming have increased, there is more emphasis placed on higher fuel economy lean-burn engines (Belton and Taylor, 1999). More lean burn fuel-efficient engines can accomplish decreased emissions of CO_2 (greenhouse gas). Hence, the lean-burn diesel and direct injected gasoline engines are logically solutions since fuel economies of >20% can be realized. Current three-way catalyst could not be employed for the removal of NO_x from lean burn gasoline and diesel engines, since the high level of O_2 are contained in the exhaust of the engine. If a lean-burn engine is to become commercially viable, novel catalyst technologies are needed. Similar catalysts may also find application for compression ignition, direct injection (CIDI or diesel) engines, where highly oxidizing conditions in the exhaust stream demand similar advances in catalyst technology.

1.2 Research Background

In this following sections, the types, sources and the emission levels of nitrogen oxides, their influence on the environmental and public health, their regulation, the approaches for their removal and the state of the art with respect to catalytic solutions for their removal is reviewed.

1.2.1 Description on Nitrogen Oxides

1.2.1.1 Origins of Nitrogen Oxides

The main source of NO_x emissions is the combustion of fossil fuels such as coal in electrical power plants or petroleum in vehicles. Table 1.1 shows the three typical types of NO_x that produced from combustion processes. The combustion gases resulting from fossil fuels contain NO_x pollutants consisting mainly have NO and NO_2, with NO representing 90 to 95% of the total NO_x (Fritz and Pitchon, 1997).

Table 1.1: Three types of NO_x that can be distinguished in flue-gas (Bosch and Janssen, 1987)

Fuel NO_x	Formed by oxidation of the nitrogen-containing compounds in the fuel and from the heterogeneous oxidation of char nitrogen in the flame tail.
Thermal NO_x	Formed by fixation of atmospheric nitrogen and its formation is thermodynamically favored by high flame temperature and atomic oxygen concentration.
Prompt NO_x	Formed by the oxidation of intermediate HCN via reaction of nitrogen radicals and hydrocarbons followed by oxidation of the HCN to NO.

NO or NO_2 formation depends on temperature, oxygen concentration, residence time or light intensity. At temperatures above 1300°C, the reaction between molecular oxygen and nitrogen introduced with air prevails. In excess of oxygen the NO formation goes according to the mechanism established by Zeldovich (Bosch and Janssen, 1987). The first step of this mechanism requires thermal dissociation of molecular oxygen and the following reactions:

$$N_2 + O^* \rightarrow NO + N^* \tag{1.1}$$

$$N^* + O_2 \rightarrow NO + O^* \tag{1.2}$$

$$\overline{\hspace{6cm}}$$

$$N_2 + O_2 \rightarrow 2NO \tag{1.3}$$

By assuming a constant concentration of N* radicals and a large oxygen content when compared to NO concentration, the following equation is obtained:

$$d[NO]/dt = 2k\exp(-E_A/RT)[N_2][O^*] \quad (1.4)$$

Equation (1.4) shows that the formation of NO is essentially controlled by reaction (1.1). It also reveals the importance of both temperature and atomic oxygen concentration. From the point of view of NO production, the oxidation of organic nitrogen compounds from fuel is not significant. Fuel NO_x formation is independent of the temperature of the flame at normal combustion conditions and insensitive to the kind of organic nitrogen compound (Bosch and Janssen, 1987).

Figure 1.2 indicates that the two primary sources of NO_x emissions are stationary-source fuel combustion and transportation. Together, these two sources comprise 94% of 2000 total NO_x emissions in the United State (EPA, 2002). Emissions from transportation sources have increased over the last 20 years (24 %) and during the past 10 years (6 %). Emissions of nitrogen oxides have increased over the last 20 years by 7 % and by less than 1 % over the most recent 10-year period from 1991 to 2000 in the United State (EPA, 2002).

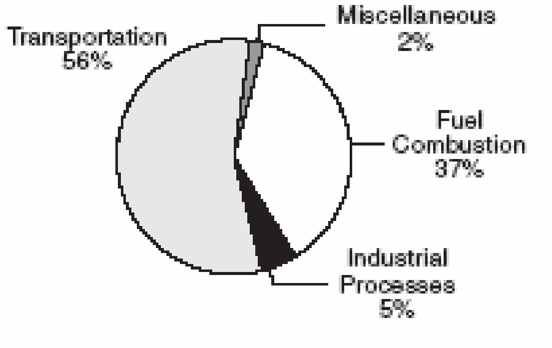

Figure 1.2 NO_x Emissions by Source Category in United State, 2000 (EPA, 2002)

1.2.1.2 Environmental and Health Related Problem

Nitrogen oxides are an extremely harmful to the environment and represent a serious hazard to the health (Bosch and Janssen, 1987; Fritz and Pitchon, 1997; and EPA, 2002). Figure 1.3 shows the chemical transformation of NO in the atmosphere and how it affects the environment. NO is the precursor for the different nitrogen oxides. Once released into the atmosphere NO undergoes chemical transformations. It is rapidly oxidized by ozone, OH or HO_2 radicals to form higher oxides of nitrogen such as NO_2, HNO_2 and HO_2NO_2.

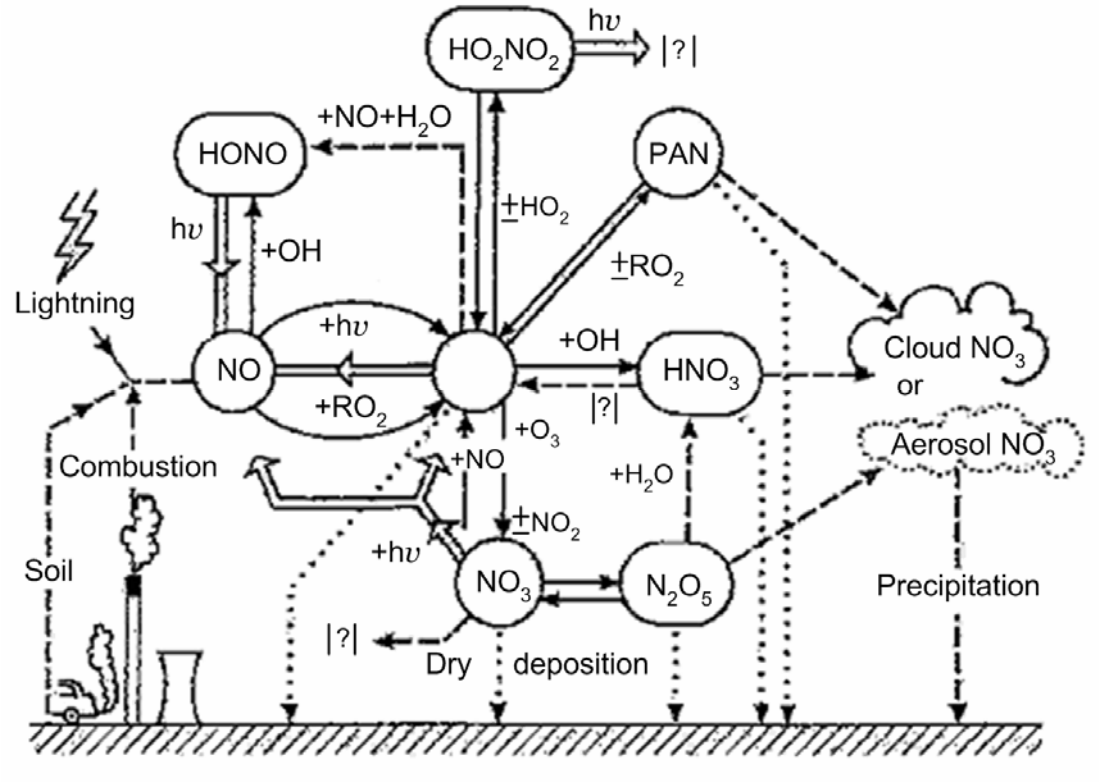

Figure 1.3 Transformations of atmospheric NO_x: (⇨) photochemical processes, (⟶) thermal gas-phase processes, (---►) heterogeneous reaction, (·······►) dry deposition (Bosch and Janssen, 1987)

NO_x reacts in the air to form ground-level ozone and fine particle pollution, which are both associated with adverse health effects (EPA, 1998). NO_x contributes to a wide range of environmental effects directly and/or when combined with other precursors in acid rain and ozone. Nitrogen, alone or in acid rain, also can acidify soils and surface waters. Acidification of soils causes the loss of essential plant nutrients and increased levels of soluble aluminum that are toxic to plants. Acidification of surface waters creates conditions of low pH and levels of aluminum that are toxic to fish and other aquatic organisms.

In the presence of air, NO is oxidized to NO_2, which is a rapid conversion at high concentrations, further accelerated in the presence of sunlight and hydrocarbon from unburned gasoline. Short-term exposures (less than 3 hours) to low levels of NO_2 may lead to changes in airway responsiveness and lung function in individuals with preexisting respiratory illnesses and increases in respiratory illnesses in children. Long-term exposures to NO_2 may lead to increased susceptibility to respiratory infection and may cause irreversible alterations in lung structure. Epidemiological studies have revealed that concentrations of nitrogen oxides having hazardous effects for people in good health are above 0.05 ppm for an exposure of over 24 hours (EPA, 2002).

1.2.1.3 Legislation Aspect

The negative impacts on the health and environment as well as economic losses caused by NO_x have resulted to stringent emissions standards imposed by environmental regulations. In 1955, an initiative to limit toxic emissions was taken in the US where clean air legislation was enacted (Armor, 1992) It was followed by the air Quality Act of 1967 and the Clean Air Amendments of 1970 and 1977. In 1990 further refinements in the pollution control were introduced. In Table 1.2 an historical overview of the limits of CO, HC and NO_x emissions from passenger cars in the US is given. It is seen that strict legislation for passenger cars was established every year to ensure significant reduction in exhaust emissions.

Table 1.2: Historical overview of the limits for emissions from passenger cars in the United States (Lox and Engler, 1999)

Year	**Area**	**Pass levels (g mile^{-1} except where stated)**		
		CO	**HC**	**NO$_x$**
1966-67	California	1.5%	275 ppm	-
1968-69	Federal & California	1.5%	275 ppm	-
1970	Federal & California	23	2.2	-
1972	California	39	3.2	3.2
	Federal	39	3.4	-
1975	California	9	0.9	2
	Federal	16	1.5	2
1980	California	8	0.41	1
	Federal	7	0.41	2
1981	Federal & California	3.4	0.41	1
1993	Federal & California	3.4	0.25	0.4

Similar to the US, legal norms for Europe are becoming tighter and tighter (see Table 1.3). For NO$_x$, subsequent European norms with interval of less than 5 years sometimes require as much as 50% reduction. The situation become such, that very sophisticated exhaust control technology will play an important role in future emissions reduction.

Table 1.3: European emission norms for private cars (Khadilkar *et al.*, 1999)

	EURO I 1992	**EURO II 1996**	**EURO III 2000**	**EURO IV 2005**
HC (g km^{-1})	0.97 (a)	0.5 (a)	0.20	0.10
CO (g km^{-1})	2.72	2.2	2.3	1.0
NO$_x$ (g km^{-1})	-	-	0.15	0.08

(a) HC + NO$_x$

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1.2.1.4 Emission Control Strategies

There are several techniques developed to control NO_x emissions. These can be classified in three categories: pre-combustion control techniques, combustion control techniques and post-combustion control techniques (Bosch and Janssen, 1987; Ismagilov and Kerzhentsev, 1990; and Latta, 1998). Pre-combustion control techniques involve removing nitrogen, which is organically bound in the fuel, through a hydrotreating process (Wojciechowska and Lomnicki, 1999). Combustion control techniques involve modifying the combustion process and/or equipment to inhibit the formation of NO_x and this is usually achieved by lowering the combustion temperature (below 1300°C) to minimize the NO_x formation through the atmospheric nitrogen fixation (Bosch and Janssen, 1987; and Ismagilov and Kerzhentsev, 1990). As mentioned above, lower temperatures of flame limit the thermal NO formation. Injection of steam, water into the combustion chamber or partial flue-gas recirculation achieves this goal and results in reduction of NO_x emissions. Pre-combustion procedures are not very expensive, but a drawback of these techniques is sometimes they enhanced N_2O formation (Armor, 1995). The main disadvantage of these methods is the low NO_x conversion (<50%) compared to post-combustion techniques (100%) (Ismagilov and Kerzhentsev, 1990; Pârvulescu *et al.*, 1998; and Wojciechowska and Lomnicki, 1999).

On the other hand, post-combustion control techniques involve injection of chemicals in specific temperature windows, in presence or absence of catalysts, to convert NO_x to N_2. Post-combustion methods are secondary measures for the treatment of the flue gas already containing NO_x. According to the environment in which they are applied secondary methods for NO_x control can be separated in wet and dry methods. The wet methods or chemical scrubbing are chemical oxidation/absorption processes that are applied to small NO_x sources and have disadvantages such as high cost and waste generation in the form of dissolved nitrates and nitrites (Ismagilov and Kerzhentsev, 1990; and Maisuls, 2000). The dry methods include catalytic and non-catalytic process. An example of non-catalytic methods is the selective non-catalytic reduction (SNCR), developed by Exxon (Altwicker *et al.*, 1999). It is a homogenous gas phase reduction process in which NO_x is selectively reduced by NH_3 to N_2. This process requires low capital investment however its temperature operation window (850-1050ºC) is very narrow and difficult to operate in larger facilities (Bosch and Janssen, 1987; Ismagilov and Kerzhentsev, 1990; and Latta, 1998). In comparison to the non-catalytic solutions, catalytic methods offer lower operating temperatures and are the primary method to control gas emissions. The possible catalytic solutions can be divided into two main categories which are direct catalytic decomposition of NO and selective catalytic reduction of NO_x using reducing agents such as ammonia, carbon monoxide and hydrocarbons.

On the other hand, a new class of prospective catalysts for the removal of nitrogen oxides from vehicle exhaust is NO_x storage-reduction (NSR) catalysts (Matsumoto, 1996; and Shinjoh *et al.*, 1998). The mechanism of NO_x adsorption and desorption/reduction is shown schematically in Figure 1.4. In lean-burn conditions, where oxygen exists in high concentration in exhaust gasses, NO_x are stored at the surface of a Ba-containing catalyst under various forms (surface nitrites/nitrates). After that, the stored NO_x species will be reduced to N_2 over Pt or more generally, TWC-type catalyst when the engine operates in the stoichoimetric or rich burn condition. In NSR catalyst, the basis of the active phase is platinum modified with alkaline earth metals and metal oxides supported on alumina. The conversion obtained is 60% and higher (Matsumoto, 1996). The major drawback of the NSR catalyst is its sensitivity to SO_x due to the fact that surface sulphates are invariably more thermally stable compared to nitrate (Engström *et al.*, 1999). However, these catalysts are still under study. Since the proposed research focuses on catalytic reduction of NO_x, a detailed review of NSR catalysts will not be included here.

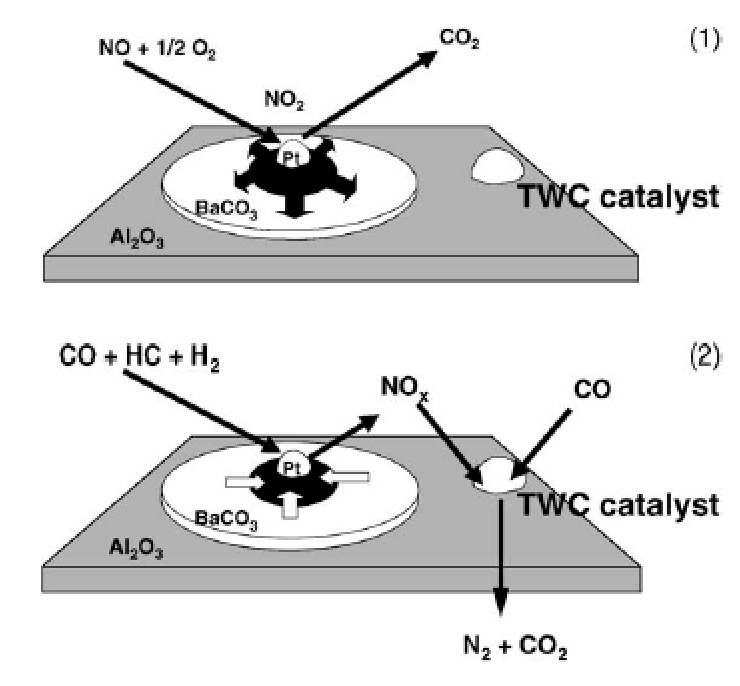

Figure 1.4 Principle of operation of an NSR catalyst: NO_x are stored under oxidising conditions (1) and then reduced on a TWC when the A/F is temporarily switched to rich conditions (2) (Kašpar *et al.*, 2003)

1.2.2 NO_x Emission Control for Lean-burn Engine

The goal for future automobile development is to have more fuel efficient and lower emission vehicles. Lean-burn engines have been identified by U.S. automakers as the next major technological step in combustion engine design and fuel economy. By using more air during combustion, lean-burn engines yield better mileage and produce less carbon monoxide and unburned hydrocarbon pollutants than conventional gasoline engines. Lean-burn engines have been developed to improve the fuel efficiency. These lean-burn engines operate at an air/fuel ratio of 18:1 or higher, which is much higher than the stoichiometric air/fuel ratio of 14.7. Engines operate under these conditions can improve the fuel efficiency by 10-15% (Shelef, 1995; Farrauto and Heck, 2001; Ménil *et al.*, 2000; and Ozawa *et al.*, 1996). This is due to:

a) Lower pumping losses
b) A higher ratio of the specific heat of the burnt gases at constant pressure to the specific heat at constant volume
c) Reduced heat losses to the walls of the combustion chamber

Besides, there is another advantage of lean-burn engine, which is the fact that the highest exhaust temperatures are typically lower (≤ 800 – 850°C) compared to the stoichiometric engine in which the exhaust temperature can go up to 1100ºC.

One great technical obstacle for the application of the lean-burn engines for the modern vehicles is the lack of a catalyst for effective emission control. Although it is very effective under the stoichiometric air/fuel ratio, the traditional three-way catalyst cannot selectively reduce NO_x in the lean-burn exhaust that contains a high concentration of O_2 (Figure 1.5). So there is an immediate need to develop catalysts, which can operate with excess oxygen (lean NO_x control) conditions to meet the NO_x standards for lean-burn engine exhaust. Table 1.4 shows the typical lean-burn exhaust compositions.

Nowadays, the challenge of lean-burn engine emission control is reducing NO_x in the presence of excess oxygen. Tabata *et al.* (1994) have reviewed the patent literatures NO_x reduction by hydrocarbon in the presence of excess oxygen. Nearly 200 patents were cited, and most of them were filed between 1987-1992. Other articles by Pârvulescu *et al.* (1998) and Shelef (1995) gave excellent reviews on the progress of fundamental research and practical development of the catalysts for lean NO_x reduction by hydrocarbon.

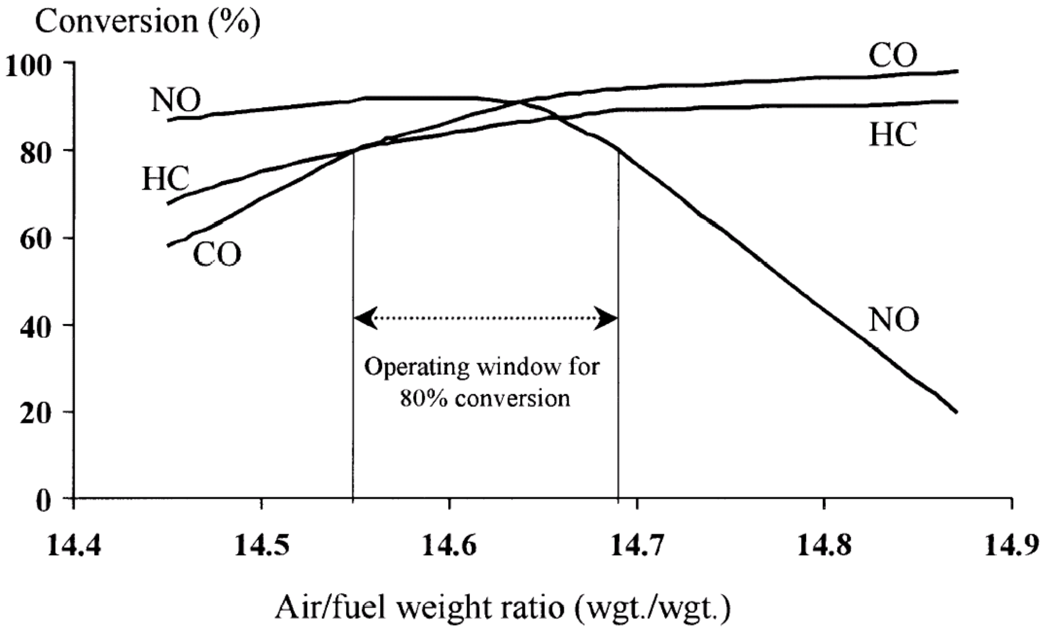

Figure 1.5 Three way catalyst performance determined by engine air to fuel ratio (Farrauto and Heck, 2000)

Table 1.4: Exhaust composition of lean-burn engine at air/fuel ratio of 18 and 22 (Kharas, 1993)

Air/fuel ratio	**NO (ppm)**	**HC[a] (ppm)**	**CO (ppm)**	**O_2 (%)**	**CO_2 (%)**	**H_2O (%)**	**H_2 (ppm)**
18	1200	1600	3000	3.2	10	10	1000
22	1200	3000	1000	7.5	9	10	330

[a] based on C_3H_6

1.2.3 Practical Considerations for Lean NO_x Reduction Catalyst

1.2.3.1 Selectivity

In lean NO_x reduction, the catalyst should be highly selective in the reduction of NO_x rather than the non-selective reduction of O_2 (combustion) in the presence of high concentration of O_2. In this study, the concept of selectivity of a NO_x reduction catalyst is represented by the competitiveness factor ($S_{SCR\text{-}HC}$), which is defined as a ratio of oxygen atoms supplied from NO to all oxygen atoms reacts with hydrocarbons to form CO and CO_2 (Shimizu *et al.*, 1998a). The following soichiometry reactions are considered:

$$C_3H_6 + 6NO \rightarrow 3CO + 3H_2O + 3N_2 \qquad (1.5)$$

$$C_3H_6 + 9NO \rightarrow 3CO_2 + 3H_2O + 9/2N_2 \qquad (1.6)$$

$$C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O \qquad (1.7)$$

$$C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O \qquad (1.8)$$

The $S_{SCR\text{-}HC}$ is equal to 100% in the case of complete selective oxidation of hydrocarbon by NO (only reactions (1.5) and (1.6) occur). The value of $S_{SCR\text{-}HC}$ decreases as the reaction between the hydrocarbon and O_2 become dominant (reaction (1.7) and (1.8)) (Amin *et al.*, 2003).

1.2.3.2 Durability

According to the new regulation, the lifetime of the automobile catalyst must be at least 100,000 miles or 10 years of engine operation (Shelef, 1995). As in most heterogeneous catalytic processes, lean NO_x reduction catalysts are also susceptible to thermal and hydrothermal. The car engine normally operates at temperatures above 400^{o}C and occasionally to 800-900^{o}C depending on the operation status. Besides, steam is an unavoidable component in the combustion exhaust. Water vapor found to be reversely suppress the fresh activity of many lean NO_x reduction catalysts (Kikuchi and Yogo, 1994). The irreversible deactivation of the lean NO_x reduction catalysts in the presence of water vapor is also very common.

1.2.3.3 Activity

The lean NO_x reduction catalysts should show good activity under various conditions depending on the operation of the engines. Two main parameters related to the catalytic activity are the width of the operating window and space velocity. The actual operating temperature of the lean-burn engine can be in a range as wide as several hundred degrees owing to the change of speed as tested by Federal Test Procedure (Yan, 1997). This requires the catalyst to remain active in a wide temperature window. Furthermore, in order to keep the volume of the catalyst used for treatment within affordable limits, the catalyst needs to be active in a range of gas hour space velocity (GHSV), from 30,000 to 100,000 hours^{-1} (Shelef, 1995).

1.2.4 Catalytic Control of NO

1.2.4.1 Direct Decomposition of NO

At low temperatures, nitric oxide is a thermodynamically unstable molecule when compared with N_2 and O_2 (Iwamoto and Yahiro, 1994). Thus, its catalytic decomposition seems to be the simplest and cheapest method to remove NO_x from exhausts gases.

$$NO\ (g) \rightarrow 1/2N_2 + 1/2O_2 \qquad \Delta G^o = -86 kJ\ mol^{-1} \qquad (1.9)$$

The direct decomposition of NO to N_2 and O_2 is an attractive option because it does not involve the use of reductant. Thermodynamically the reaction is favorable up to 1000^{o}C; however, due to its high activation energy of NO decomposition (364 kJ mol^{-1}) makes it necessary to use a catalyst (Fritz and Pitchon, 1997).

Many papers have been devoted to the catalytic decomposition of nitric oxide over noble metals, transition metal oxides and zeolite (Lee *et al.*, 1994; and Iwamoto, 1996). It is widely accepted that the active centers of metal oxide catalysts for NO decomposition are the oxygen defects on the surface. Hamada *et al.* (1990) have shown that, by adding silver to cobalt oxide, both activity and resistance to oxygen poisoning are increased. Namely, they reported that the oxide catalysts bonded the oxygen atoms formed during NO decomposition, which resulted in catalysts deactivation. The additive effect of silver would be due to weak affinity of silver for oxygen.

Perovskite-type oxides have also been investigated for this reaction (Zhao *et al*., 1996; and Wu *et al*., 2000). The advantages of these catalysts are their extreme thermal stability (Iwamoto, 1994) and they permit easy desorption of a large amount of oxygen from oxide bulk, thereby implying that inhibition by oxygen would not be extensive (Fritz and Pitchon, 1997). Unfortunately, the surface areas of these catalysts are low (Iwamoto, 1994).

The most promising results for the NO decomposition were obtained on the high-silica zeolite catalysts containing copper ions (Iwamoto and Yahiro, 1994; Li and Hall, 1990; and Schay *et al*., 1998). Unfortunately, the most promising systems for NO decomposition, such as Cu-ZSM-5, do not suppress the inhibiting effect of oxygen. The presence of water vapor also has an inhibiting effect on the NO decomposition and the deactivation is usually irreversible as it affects the very framework of the zeolite (Fritz and Pitchon, 1997).

1.2.4.2 Selective Catalytic Reduction of NO by Ammonia (SCR-NH_3)

No such catalyst exists today which is capable of decomposing NO_x according to reaction (1.10). So an alternative approach is to catalytically reduce NO_x selectively using reducing agents. The most common catalytic procedure for selective catalytic reduction (SCR) is using ammonia or ammonia-containing compounds, mainly urea, as reducing agents. The process was discovered first by Cohn in 1961 (Cohn *et al*., 1961). It is the most effectively applied catalytic method of NO_x reduction in conventional electric power plants (Shelef, 1995). Lean-NO_x engine manufacturers are also considering the use of NH_3 as the reductant for NO_x

for heavy duty truck. Urea is convenient for on board use as liquid carrier for ammonia. It hydrolyzes in the exhaust system according to reaction (1.10).

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (1.10)$$

The NH_3 will then react selectively with NO_x (Equations (1.11) and (1.12)) to give conversions ranging between 80 and 90%.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1.11)$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (1.12)$$

although other undesired reactions also may occur. Such undesired reactions are the oxidation of NH_3 to N_2 (1.13) or NO (1.14). Another side reaction involves the reduction of NO_x to N_2O.

$$4NH_3 + 3O_2 \rightarrow N_2 + 6H_2O \qquad (1.13)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1.14)$$

An excellent review by Bosch and Janssen (1987) on different types of catalysts investigated for use in the $DeNO_x$ process appeared in the late 1980s. The active component is selected mainly from tungsten, molybdenum and vanadium oxides, whereas the support is usually TiO_2, Al_2O_3, SiO_2, zeolites and various combinations of these oxides (Radojevic, 1998; and Pereira and Phumlee, 1992). The temperature of activity for these catalysts varies in the 200-550ºC range according to conditions. The active sites seem to be the $(V{=}O)^{2+}$ groups in the case of vanadia catalysts (Ciambelli *et al.*, 1992). The presence of gas-phase oxygen enhances the catalyst activity and this effect is more pronounced at higher vanadia loading. Two mechanisms have been proposed for this reaction:

- The Eley-Redeal mechanism which involves the direct reaction between absorbed ammonia molecule and gaseous NO (Jansen *et al.*, 1987), while oxygen regenerates the active sites as described:

$NH_3 + s \rightarrow [s\text{-}NH_3]$ (1.15)

$[s\text{-}NH_3] + NO \rightarrow [s\text{-}H] + N_2 + H_2O$ (1.16)

$2[s\text{-}H] + 1/2O_2 \rightarrow 2s + H_2O$ (1.17)

- The formation of a reaction intermediate nitrosoamine (Turfano and Turco, 1993); here again, the role of oxygen is to regenerate the active site:

$NH_3 + s \rightarrow [H\text{-}s\text{-}NH_2]$ (1.18)

$NO + [H\text{-}s\text{-}NH_2] \rightarrow [H\text{-}s\text{-}NH_2\text{-}NO]$ (1.19)

$[H\text{-}s\text{-}NH_2\text{-}NO] \rightarrow [s\text{-}H] + N_2 + H_2O$ (1.20)

$2[s\text{-}H] + 1/2O_2 \rightarrow 2s + H_2O$ (1.21)

The SCR by the ammonia method has found many applications in Japan, Germany and USA since the early 1970s, when it was applied for the first time. SCR-NH_3 has a few advantages with NO_x reduction efficiency being the most obvious, together with the well-known and comparatively simple reaction system. The disadvantages of this method include the need for a reducing agent to be temporarily stored on board the vehicle and for which there is yet no infrastructure for supply. High costs of the SCR-NH_3 installations are also a disadvantage. Furthermore, SCR-NH_3 systems may show ammonia slip, which can produce additional environmental pollution. Due to these reasons, the use of ammonia in vehicles is somewhat controversial (Armor, 1992; and Armor, 1995).

1.2.4.3 Selective Catalytic Reduction of NO by Hydrocarbon (SCR-HC)

Hydrocarbon was found to be also effective for NO reduction under lean conditions over Cu-ZSM5 in 1990 (Iwamoto and Hamada, 1991). The use of hydrocarbon is very attractive because it can be applied for both mobile and stationary sources. Although Cu-ZSM5 is not a practical catalyst because of its lack of hydrocarbon stability, other systems have been studied extensively in an attempt to find an effective lean NO_x reduction catalyst.

The field of application of metal oxide catalysts for SCR-HC is still to be explored. In particular, the latest results indicate that the metal oxide catalysts can be as active as zeolite systems in the SCR-HC process. For example, Shimizu *et al.* (1998b) revealed that the activity of Ga_2O_2 supported alumina, in SCR process with CH_4, is similar to that of Ga-ZSM5 and its selectivity is even higher that of Co-ZSM5. Besides, Ga_2O_3/Al_2O_3 is highly resistant to the presence of moisture in the reactant gases.

The biggest challenge in lean NO_x reduction catalyst is the need to selectively reduce NO with hydrocarbon in the presence of an excess amount of oxygen and the competing reactions of hydrocarbon oxidation:

NO reduction: $NO + HC \rightarrow N_2 + CO_x + H_2O$ (1.22)
Hydrocarbon oxidation: $O_2 + HC \rightarrow CO_x + H_2O$ (1.23)

The competition can be expressed by a competitiveness factor, which can be used to compare the activities for NO reduction and for hydrocarbon oxidation of a catalyst. It is defined as the ratio of the rate of hydrocarbon conversion to produce N_2 (i.e. the rate of N_2 formation) to the rate of total hydrocarbon conversion. In addition, a practical catalyst should maintain its high activity and selectivity over a wide temperature range in the presence of water and SO_2, as well as its structural integrity at high temperatures. Because of these stringent requirements, no practical catalyst has been developed for this application yet.

1.3 The Statement of Problems

The selective reduction of NO_x during lean exhaust mixture conditions has proved a challenging problem, which, particularly during the last five years, automobile manufacturers have shared with many research laboratories. The resulting large number of publications serves both academic and applied interests. Equally, a terrific number of catalysts, in continuing association with and developed from differing technologies, do not appear to meet the requirements in real exhaust application. Many researchers are still competing to create a better $DeNO_x$ catalyst due to several problems as below:

1. Lean burn engines operate at an air/fuel ratio of 18:1 or above, which is much higher than the stoichiometric air/fuel ratio of 14.7. The current three-way catalyst is not able to reduce NO_x in the lean burn exhaust that contains a high concentration of O_2.
2. Cu-ZSM-5, under certain experiment conditions, exhibits a good activity and high selectivity towards nitrogen in the lean burn engine. However, these catalysts are subject to hydrothermal deactivation and are only active at temperatures too high to be considered for real applications.
3. Most of the current research is directed at the use of modified zeolite or simple metal oxides. Clearly simple extensions of these current approaches have not and probably will not lead to satisfactory solutions. Therefore, the focus of research needs to shift to more complex catalyst compositions.

Recently some publications have reported the drastic enhancement of NO reduction activity by the combination of two (or more than two) catalytic species. In this study, Cu is the primary active component in the CeO_2-ZrO_2 catalyst while Ag is the secondary component functioning mainly as promoter. The selection of Ag as promoter is due to the previous study done by other researchers (Chajar *et al.*, 1998 and Amin *et al.*, 2004). Amin *et al.* (2004) reported that the loading of Ag into Cu/CeO_2 catalyst enhanced a better metal dispersion and eliminate the formation of nitrous oxide (N_2O). It is believed that the addition of Ag into Cu/CeO_2-ZrO_2 catalyst will improve the catalytic performance of the catalyst in SCR-NO reaction.

1.4 Objectives

The objectives of this thesis are:

1. To prepare and characterize CeO_2, CeO_2-ZrO_2, Cu/CeO_2, Cu/Ag/CeO_2 and Cu/Ag/CeO_2-ZrO_2 catalysts.
2. To investigate the effect of Ag loading on the catalytic performance of Cu/CeO_2 catalyst for SCR of NO by C_3H_6.
3. To examine the influence of different supports over SCR of NO by C_3H_6 by comparing the catalytic performance of Cu/Ag/CeO_2 and Cu/Ag/CeO_2-ZrO_2 catalysts.
4. To conduct a detailed parametric studies of the optimal catalyst.
5. To perform a kinetic study of SCR of NO by C_3H_6 over the optimal catalyst and elucidate the mechanism of this reaction on this catalytic system.

1.5 Scope of the Study

This study consists of three parts. The first is to examine the effect of different Ag loading on the catalytic performance of Cu/CeO_2 catalysts. The optimal Ag loading was determined by varying the Ag loading on the Cu/CeO_2 catalyst from 0 – 3 wt% and tested in the NO reduction activity over a temperature range of 250 - 550ºC. The influence of different composition of CeO_2-ZrO_2 catalysts on the SCR of NO activity were examined at 400ºC in the second part of this study. Afterward, the catalytic activity of Cu/Ag/CeO_2-ZrO_2 catalyst was compared with Cu/Ag/CeO_2 over a temperature range of 250 - 550ºC to examine the effect of ZrO_2 loading onto the ceria-based catalyst.

All the synthesized catalysts in the first and second parts of this study were prepared by conventional impregnation method and were characterized with X-ray diffraction (XRD), Nitrogen Adsorption (NA), Temperature Programmed Reduction (TPR) and UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS). The performance of each synthesized catalyst was investigated in a lab-scale fixed bed reactor at atmospheric pressure. A simplified synthetic exhaust gas comprising of NO (2000 ppm), C_3H_6 (2000 ppm), O_2 (10%), H_2O (10%) if present and He (remainder) were fed to the catalyst bed at F/W = 30,000 ml g^{-1} $hours^{-1}$. The concentration of NO was analyzed with a NO_x emission analyzer, while the compositions of other products were analyzed by using a gas chromatograph equipped with a TCD detector.

Finally, steady-state kinetics experiments were conducted over Cu/Ag/CeO_2-ZrO_2 catalyst in the third part of this study. The experiments in this part were performed in a differential reactor where a bed consisting of a smaller amount of catalyst (0.25 g) was employed to control the NO conversions at <20% in most cases. The NO conversion rate dependence on the concentration of NO, C_3H_6 and O_2 were determined at 350 and 400ºC and a simplified NO reduction mechanism was proposed based on the kinetic results.

concentrations, and nearly half-order with respect to O_2 concentration. These results suggested that the NO conversion was strongly depended on the NO and C_3H_6 concentration, and the dissociatively adsorbed O_2 was important for the activation of NO and C_3H_6. Based on the kinetic expressions from the homogeneous model, a Langmuir-Hinshelwood kinetic model which satisfactorily fit the experimental data has been developed. It is proposed that the reduction process proceeded via the reaction of surface oxygenated hydrocarbons formed by the partial oxidation of gaseous C_3H_6 with the adsorbed NO_x species.

6.2 Recommendations

1. Detailed FTIR adsorption-desorption studies with various gases recommended using $Cu/Ag/CeO_2$-ZrO_2 catalyst. These studies will provide information about intermediates as well as about oxidation state changes of Cu and Ag. Therefore, these studies can be used to elucidate the proposed promotion effect and reaction pathways on this catalyst.

2. The addition of water vapor negatively impacted the NO_x reduction performance with C_3H_6. Certain types of higher hydrocarbons are more reactive by their capability to generate the critical active hydrocarbon intermediate. These types of hydrocarbon need to be investigated to determine the impact of water vapor in the suppression or generation of the correct hydrocarbon intermediate.

3. Finally, the catalyst needs to be tested under real lean-burn exhaust. Firstly, the influence of O_2 on the catalytic performance needs to be studied extensively in view of the fact that it is plentiful in the lean-burn engine. Then, the effect of SO_2 on the catalytic activity is worthy to be studied since it is characterized as a poison due to its ability to deactivate catalyst. The influence of co-existence of other hydrocarbons in the exhaust gas such as CH_4, C_2H_4 and CO on the catalytic performance of catalyst should be also investigated.

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