

CHAPTER II

LITERATURE REVIEW

This chapter will give the background and chemistry of the reactant and sol-gel synthesis used in this work. After that, it will describe catalytic NO_x removal techniques. Past and recent works are reviewed simultaneously as well as the reaction mechanisms.

2.1 NO_x Background

The main oxides of nitrogen appear in the atmosphere are nitric oxide (NO), nitrogen dioxide (NO₂) and nitrous oxide (N₂O). NO is moderately reactive, colorless and odorless while NO₂ is highly reactive toward oxidation and reddish brown color with pungent odor. N₂O is commonly known as laughing gas. It is colorless with slightly sweet odor. However, nitrous oxide presents relatively in much less quantity. The other two, nitric and nitrogen dioxide are generally combined in term of NO_x emitted mainly from various sources through combustion processes.

2.1.1 NO_x Formation

NO_x is formed through three mechanisms: Thermal NO_x, Fuel NO_x, and Prompt NO_x as the following details.

2.1.1.1 Thermal NO_x or Zeldovich NO_x

In thermal NO_x process, the reactions occur at high temperature, usually above 1,600 K. Both molecular N₂ and O₂ in the combustion air are dissociated into their respective atomic states N and O which subsequently create thermal NO_x. It is described by the Zeldovich reactions (Bosch and Janssen, 1987) as follows:



The reaction rate is controlled by oxygen concentration and temperature. The maximum thermal NO_x production occurs at a slightly lean fuel mixture ratio due to the excess availability of oxygen for reaction within the hot flame zone. Even though the thermal NO_x formation rate is slow compared to other combustion reactions, it contributes to the largest portion to the total NO_x formed (Glarborg *et al.*, 1986).



Additionally, the hydroxyl radical can be an oxidant in fuel rich mixtures.

2.1.1.2 Fuel NO_x

The process is the oxidation of nitrogen-containing compound in the fuel such as coal, coke and heavy oils. The formation can be described as follows (Gómez-García *et al.*, 2005):



where

C(N) = nitrogen in char

I(N) = nitrogen-containing intermediate species (CN, HCN, NH and NH_2)

Fuel bound nitrogen is first converted to fixed nitrogen compounds such as HCN and NH_3 which are subsequently oxidized to NO_x . These reactions occur at relatively low temperature than that of Zeldovich mechanism. In contrast with the thermal NO_x , the formation of fuel NO_x is independent of the flame temperature and insensitive to the type of organic nitrogen compound (Bosch and Janssen, 1987).

2.1.1.3 Prompt NO_x or Fenimore NO_x

Prompt NO_x is formed according to Fenimore mechanism. The hydrocarbon fragments such as C, CH, and CH_2 may react with atmospheric

nitrogen under fuel rich conditions and subsequently produce fixed nitrogen species such as CN, H₂CN, HCN and NH. Afterwards, these intermediates are oxidized in lean zone to form prompt NO_x. Its formation is proportional to the number of carbon atom (Roy *et al.*, 2009) and can occur at a much lower temperature than thermal NO_x i.e. 1,000 K. However, only small fraction of the total NO_x is produced through this mechanism.

In summary, lean conditions suppress prompt NO_x whereas low temperatures suppress thermal NO_x. Normally, thermal NO_x is the main mechanism in engines and boilers with diesel, gasoline and gas fuels. Contrarily, in coal power plants, fuel NO_x is usually the major route for NO_x formation. The principle of catalytic NO_x removal is to reverse the reactions of NO_x forming at a lower corresponding temperature.

2.1.2 NO_x Thermodynamics and Kinetics

In a thermodynamic point of view, nitric oxide and nitrogen dioxide are unstable (Gómez-García *et al.*, 2005).



On the other hand, kinetics studies have revealed that the decomposition is inhibited by its high activation energy barrier; ~335 kJ/mol for NO decomposition (Garin, 2001). The uncatalyzed reaction proceeds very slowly until it reaches very high temperature; >2,000 K (Grassian, 2005). Anyway, at low temperature NO can react with oxygen to form NO₂ but it fully shifts to the left at high temperature as described by Equation (1.9). Figure 2.1 shows the thermodynamic stability of NO₂ as a function of temperature for the partial pressure of oxygen between 0.01 and 0.20 atm. It illustrates that NO₂ is stable at low temperatures while NO is more stable than NO₂ at high temperatures. In addition, the stability of NO₂ in the gas phase increases with increasing partial pressure of oxygen.

At low temperatures, NO can also be converted to N₂O. This reaction; which is shown in Equation (1.10), is unfavored at high temperature. Hence, N₂O can be an intermediate in the reduction of NO to N₂ at low temperatures (but not necessarily is). At high pressures and low temperatures, NO is unstable. It is disproportionate to N₂O and NO₂ as shown in Equation (1.11).



Busca *et al.* (2005) noted that the equilibrium dimerization of NO is likely an intermediate step in the reactions (1.9) to (1.11). As mentioned above, the decomposition of NO could not proceed spontaneously because of its high activation energy. The use of different reductants in NO reduction to nitrogen as below reactions could be an accomplished option.



However, these reactions require the catalysts performing selectively without N₂O formation at low temperature. Three-way catalysts (TWCs) used for gasoline engines applied CO as a reducing agent working in approximately stoichiometric condition of air to fuel mass ratio at 14.7, which is designated as $\lambda = 1$. Contrarily, ammonia is employed for stationary sources in oxidizing condition. Methane as its abundant natural gas is an alternative for ammonia in industrial plants but it is still not commercialized. The use of hydrogen is not attractive because it is not practical in oxygen excess condition.

Although N_2O is more stable than NO at low temperature, its formation is also thermodynamically favored at high temperature through oxidation processes such as the equations shown below. As well as NO , the decomposition of N_2O is thermodynamically favored but it is obstructed by kinetic reasons. However, it is quite efficient over catalysts at high temperature so the reduction of N_2O to nitrogen by reducing agents is not attractive.

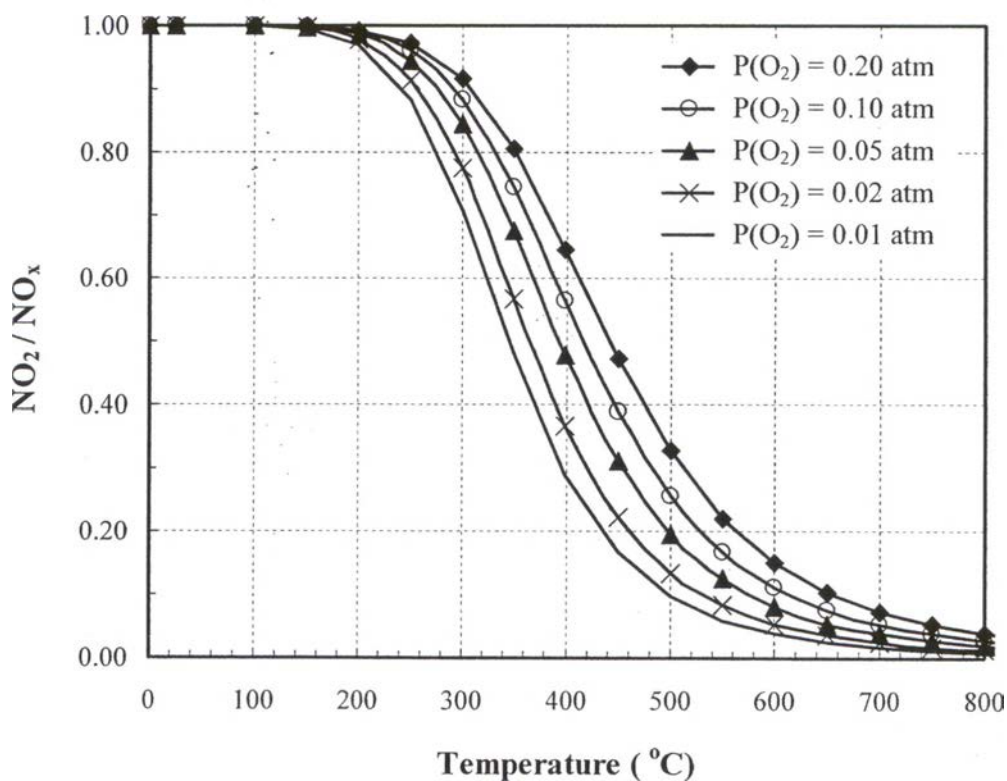


Figure 2.1 The thermodynamic equilibrium fraction of NO_2/NO_x as a function of temperature in different partial pressures of oxygen.

2.1.3 NO_x Surface Chemistry

Nitric oxide, NO is considered as a radical molecule. It has an unpaired electron in its $2\pi^*$ orbital. For this reason, NO owns paramagnetic property. Its bond length is 1.15 Å which is intermediate between triple bond distance in NO^+ of 1.06 Å and double bond ~ 1.20 Å (Roy *et al.*, 2009). When it exposes to metal surface, NO can either donate its unpaired electron to the surface like CO or accept electron from the surface into the partial $2\pi^*$ orbital. Therefore, it can adsorb on the surface in various geometries such as linear (atop), bent, bridge, and etc. as shown in Figure 2.2. Additionally, it interacts with the substrates via N or O.

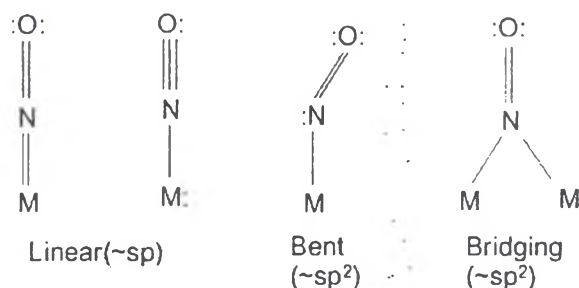


Figure 2.2 Schematic representation of the bonding in NO complexes (Brown and King, 2000).

In a metal-NO bonding, NO creates a 5σ -d bond with metal atoms like in M-CO. Then back bonding takes place from d orbital of surface metal to $2\pi^*$ orbital of NO. If NO receives an electron in its antibonding orbital, it becomes NO^- which is isoelectronic to O_2 . O_2 adsorption always forms a side-on geometry that further dissociates to form $\text{M}=\text{O}$. Similarly, when adsorbed NO becomes NO^- , it transforms to a side-on geometry and then dissociates as illustrated in Figure 2.3. If the metal surface is promoted by alkali metal or alkaline-earth metal, it will lead to an extra electron on the metal surface. Then the charge transfer from metal d orbital to NO $2\pi^*$ orbital should increase. Accordingly, it promotes NO dissociation.

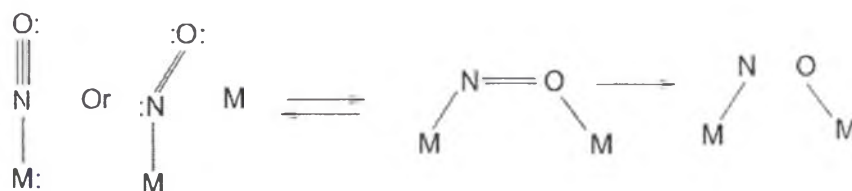
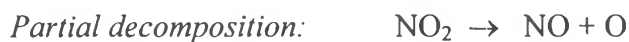


Figure 2.3 Schematic representation of NO dissociation (Palermo *et al.*, 1996).

Nitrogen dioxide, NO_2 is a radical and a strong oxidizing agent. It can bond with the surface metal as a ligand through N, O end or a combination of N and O atom. Then NO_2 can transform through various reactions. Anyway, NO_2 adsorption as molecular has been observed as well.



Nitrous oxide, N_2O is a triatomic molecule with asymmetric shape (NNO). It required relatively small energy for N–O bond cleavage; ~ 40 kcal/mol (Rodriguez *et al.*, 2001). Consequently, dissociated adsorption to gaseous N_2 and O adatom is not difficult. However, the molecular adsorption is also present.

2.2 Sol-gel

The sol-gel route proceeds via sol formation followed by gel formation. Sol is one type of the colloidal states which are the state that colloidal particles ranging from 1 to 1,000 nm in size suspended in the second phase. The colloidal suspension of a solid in a liquid phase called sol can be obtained by the hydrolysis and partial condensation of precursor. The further condensation of sol results in a three-dimensional polymeric network of gel. The porous materials obtained after drying process are used for many applications such as ceramic material, and catalyst preparation. The important characteristic of the sol-gel technique in catalytic

application is its availability to control chemical and physical properties of product (Ertl *et al.*, 1999).

- Maintain high purity
- Be able to control physical characteristics such as pore size distribution and pore volume
- Give homogeneous content in molecular level
- Can introduce several components in a single step
- Be able to produce samples at low temperature

2.2.1 Sol-gel Chemistry

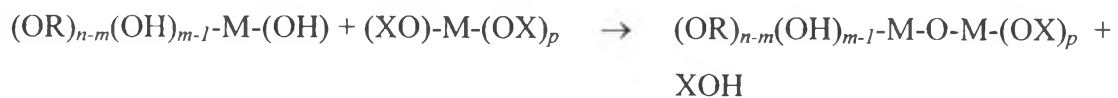
Generally, there are two routes in sol-gel preparation depending on the chemical nature of precursors. One is the aqueous route which is based on inorganic salts dissolved in water. The other is the metal-organic route which is based on alkoxides dissolved in organic solvents (Livage, 1998). Among these starting materials, metal alkoxides have been the most extensively used because of their commercial availability in high purity.

The sol-gel chemistry of metal alkoxide ($M(OR)_n$) can be described in terms of the following reactions (Ward and Ko, 1995):

Hydrolysis:



Condensation:



where

X can be either H or R (an alkyl group)

n , m , and p are the numbers of hydroxyl or alkoxy groups

2.2.2 Drying Process

The encapsulated solvent in gel can be removed by either evaporative drying or supercritical extraction resulting in a xerogel or an aerogel, correspondingly. As the solvent evaporates, a liquid-vapor interface develops inside a pore. The surface tension along with capillary pressure acts on the walls of pores consequent in pore structure collapse during drying process. Therefore, in order to maintain the pore size and pore volume, various techniques have been employed to prepare uniform pore gels or remove the liquid-vapor interface through the drying process (Kung and Ko, 1996). There are a number of general drying methods.

2.2.2.1 *Evaporative Drying*

The removal of the aqueous/alcohol solvent is proceeded at low pressure and above boiling point of the solvent. The resulting materials termed xerogel have high surface area but are usually microporous.

2.2.2.2 *Supercritical Drying*

a) High temperature supercritical drying

The solvent is removed under supercritical condition. At this condition, the vapor-liquid interface disappears leading to no surface tension to collapse the pores. Hence, the obtained material called aerogel can be maintained large pore size and pore volume. In this method, drying temperature and pressure must be higher than the critical point of the solvent to reach identical properties of liquid and vapor phase.

b) Low temperature supercritical drying

This technique is the exchanging of the solvent with supercritical CO₂. The vapor-liquid interface is removed initially by mixing the solvent with supercritical CO₂ that can be named as CO₂ extraction. Since the critical temperature and pressure of CO₂ are lower than those of aqueous or alcohols, it gives safer operating conditions.

2.3 Catalytic NO_x Control

Several technical challenges remain for improving the catalytic reaction to its application in NO_x control for stationary and mobile source emissions. The

catalyst must be optimized for high activity at low operating temperature of 350-500 °C during warm up conditions in gasoline engine or as low as 200-300 °C in light duty diesel applications (LDD) and at high space velocities condition in flue gases. Since combustion exhaust streams contain high level of water (10-16%), the thermal and hydrothermal stability is a crucial part for a successful catalyst. In addition, diesel and natural gas contain sulfur components so the critical issue of SO_x resistance of the catalyst must be addressed.

2.3.1 NO_x Decomposition

The fact that nitric oxide is thermodynamically unstable relative to N₂ and O₂ at low temperature has attracted scientists to use catalyst for the direct NO decomposition as described in the equation (1.7). This approach is the simplest and the most desirable in NO removal because it does not require any reducing agents. In the 1970s, it was widely known that catalytic decomposition was inhibited by the presence of oxygen. In order to accomplish NO decomposition, oxygen desorption must occur at temperature lower than 773 K. Iwamoto *et al.* (1977, 1982, 1986) have first discovered that copper ion-exchanged zeolites are active for NO decomposition. This work ultimately resulted in the breakthrough that Cu-ZSM-5 was capable to decompose NO significantly when compared with other traditional catalysts. Unfortunately, the most promising catalyst Cu-ZSM-5 is not very stable in humid conditions even to 2% water content over extended time on stream. Its activity also is inhibited by SO₂ as it competes with NO for the adsorption sites and consequently prevents the catalytic reaction. The deactivation is usually irreversible because both water and SO₂ can destroy the framework structure of zeolites.

Perovskite-type oxides have also been studied in this catalytic NO decomposition (Halasz *et al.*, 1991; Tofan *et al.*, 2002; Ishihara *et al.*, 2003). This type of mixed oxides is a possible candidate in the decomposition because its defect oxides allow easily desorption of oxygen from the oxide bulk. It implies that oxygen inhibition effect would not be dominant. Furthermore, the advantage of these perovskite oxides is their stability in the structure at high temperatures. Conversely, the disadvantage is its low surface area due to high temperature required in its preparation. No significant activity in NO decomposition under the conditions in

automotive catalytic converters have been reported so far. Goralski *et al.* (2002) concluded that lean burn NO_x control with respect to catalytic decomposition in automobile is practically impossible after they applied free energy minimization calculations to analyze the thermodynamic feasibility of NO_x decomposition catalyst.

Most previous attempts to develop practical decomposition catalysts have been studied in noble metals and metal oxides. Some of them are active in the reduced state. However, oxygen contained in the feed gas or released from NO decomposition competes with NO for the adsorption sites and ultimately poisons the catalysts. It requires high reaction temperatures and/or reducing agents to remove surface oxygen and restore the catalytic activity. Therefore, catalytic reduction processes using CO, hydrogen, hydrocarbons or nitrogen-containing compound such as NH₃ and urea have been applied for NO_x removal. These processes through both selective and non-selective methods are used in industrial boilers and vehicle engines, respectively.

2.3.2 Selective Catalytic Reduction with Hydrocarbons

A typical composition of the exhaust emitted from lean-burn engines contains about 0.05% NO_x, 5-10% O₂, 10% H₂O and 0.05-0.1% hydrocarbon (Kung *et al.*, 1996). Therefore, the hydrocarbons present in the exhaust gas are sufficient to completely reduce NO_x to N₂ if they are not consumed first by oxygen through their combustion. Since Iwamoto *et al.* (1991) and Held *et al.* (1990) reported that selective reduction of NO_x by hydrocarbons proceeded under lean-conditions over Cu-ZSM-5 catalyst in early 1990s, the selective catalytic reduction of NO_x by hydrocarbons has been studied extensively over ion-exchanged zeolites, metal oxide and noble metal catalysts.

Both of the metal oxide and zeolite based catalysts exhibit poor lower temperature activity. In contrast, noble metal catalyst is active at low temperature regions. It was reported by Obuchi *et al.* (1993) that Pt/Al₂O₃ catalyst was active at about 250 °C with a narrow temperature window. For Ru/Al₂O₃ and Rh/Al₂O₃ catalysts, the temperature shifted to higher temperature and became wider. In contrast, the activities of Pd/Al₂O₃ and Ir/Al₂O₃ were very poor. This indicates that the activity of the noble metal catalyst is also closely related to the supported metal.

Since the noble metal catalyst shows relatively better resistance against SO_2 compared to the metal oxide catalysts (Efthimiadis *et al.*, 1998), improving the low selectivity to N_2 is the most important research target. Among the platinum group metal (PGM) catalysts, Pt catalyst is the most attractive one and has been widely studied (Burch and Scire; 1994, Burch and Ottery; 1997, Burch and Watling; 1997; Burch *et al.*, 2002; Ingelsten *et al.*, 2003). However little research has been reported about the relationship between the activity and the microstructure of Pt catalyst. It was found that relatively large platinum particle size shows a positive effect on the catalytic de NO_x activity (García-Cortés *et al.*, 2003). The main disadvantage of low selectivity toward N_2 by forming undesirable product N_2O over PGM catalyst is still opened for research. Besides this, the narrow activity temperature window is another obstacle.

Some researches on the gold catalyst for the selective reduction of NO_x was carried out (Ueda *et al.*, 1997; Ueda and Haruta, 1998; Seker and Gulari, 2002). The selectivity to N_2 over gold catalyst is satisfied in comparison to that of PGM catalysts. Ueda *et al.* (1997) found that $\text{Au}/\text{Al}_2\text{O}_3$ prepared from the deposition-precipitation method was active, while Seker and Gulari (2002) reported that the active gold catalyst could also be prepared by the sol-gel method. The major problem for gold catalysts is the poor low temperature activity.

2.3.3 Selective Catalytic Reduction with Ammonia and Urea

Selective catalytic reduction of NO_x with NH_3 under lean conditions is a widely commercialized technology for NO_x removal from stationary sources. For this reaction V_2O_5 , WO_3 and MoO_3 are the traditional active metal oxides. For examples, $\text{MoO}_3/\text{TiO}_2$ catalyst showed relatively high activity which increased with increasing the MoO_3 loading while the N_2 selectivity decreased due to the formation of undesired N_2O (Nova *et al.*, 1998). The 10%Fe-10% Mn/ TiO_2 catalyst is substantially more active than all other catalysts reported in the literature. Nearly 100% of NO_x conversion is obtained at 120 °C. Moreover, it shows good resistance against H_2O and SO_2 (Qi and Yang, 2003). For automotive sources, NH_3 slip and manipulation of NH_3 together with NH_3 corrosion remain the major obstacles to the use of this technology. To overcome the difficulties associated with ammonia, urea

was used as alternative reducing agent because it is safer and can generate in-situ ammonia.

The selective catalytic reduction using urea as a reducing agent has been investigated in detail for about 10 years. It is presently considered as the most promising way to diminish NO_x emissions originating from heavy duty vehicles (Koebel *et al.*, 2000). SCR technology using urea as a reducing agent for diesel engine also has been proposed by Held *et al.* (1990). They addressed some remaining problems such as low space velocity activity and narrow temperature window of the catalyst.

Koebel *et al.* (1996) has illustrated the chemistry of urea. Urea is usually applied in the form of an aqueous solution. Ammonia could be regenerated in-situ by hydrolysis and decomposition of urea through the following reactions:

1. Urea is thermally decomposed (pyrolyzed) into ammonia and isocyanic acid.



2. The isocyanic acid formed may react with water and also lead to ammonia.



It seems that urea, as ammonia source, is the best choice for such applications because of its non-toxicity and the feasibility of transportation with automobile. At present, urea-SCR is considered to be the most promising method for the heavy-duty diesel vehicles. NO_x can be reduced not only with ammonia but also the urea itself and its decomposition by-product, HNCO (Seker *et al.*, 2002) as shown in Table 2.1. It shows the main SCR reactions summarized by Fang and DaCosta (2003). They can be categorized as desirable and undesirable reactions as well as undesirable degradation. Undesirable NH₃ oxidation with oxygen or NO not only consumes ammonia required for SCR process but also produces additional NO_x by-products.

Table 2.1 Urea-SCR reactions

| | | | |
|---------------------------------------------------------------------------|---------------|------------------------------------------------------------|------------------|
| 1. Desirable reduction | | | |
| $4\text{NH}_3 + 4\text{NO} + \text{O}_2$ | \rightarrow | $4\text{N}_2 + 6\text{H}_2\text{O}$ | (standard SCR) |
| $4\text{NH}_3 + 6\text{NO}$ | \rightarrow | $5\text{N}_2 + 6\text{H}_2\text{O}$ | |
| $8\text{NH}_3 + 6\text{NO}_2$ | \rightarrow | $7\text{N}_2 + 12\text{H}_2\text{O}$ | |
| $4\text{NH}_3 + 2\text{NO}_2 + 2\text{NO}$ | \rightarrow | $4\text{N}_2 + 6\text{H}_2\text{O}$ | (fast SCR) |
| $4\text{HN}=\text{C}=\text{O} + 6\text{NO}$ | \rightarrow | $5\text{N}_2 + 2\text{H}_2\text{O} + 4\text{CO}_2$ | |
| 2. Direct urea reduction | | | |
| $2(\text{NH}_2)_2\text{C}=\text{O} + 6\text{NO}$ | \rightarrow | $5\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2$ | |
| 3. Undesirable reaction/oxidation | | | |
| a) Undesirable products | | | |
| $2\text{NH}_3 + 8\text{NO}$ | \rightarrow | $5\text{N}_2\text{O} + 3\text{H}_2\text{O}$ | |
| $4\text{NH}_3 + 4\text{NO} + 3\text{O}_2$ | \rightarrow | $4\text{N}_2\text{O} + 6\text{H}_2\text{O}$ | |
| b) Ammonia oxidation | | | |
| $4\text{NH}_3 + 3\text{O}_2$ | \rightarrow | $2\text{N}_2 + 6\text{H}_2\text{O}$ | (mild oxidation) |
| $4\text{NH}_3 + 4\text{O}_2$ | \rightarrow | $2\text{N}_2\text{O} + 6\text{H}_2\text{O}$ | (mild oxidation) |
| $4\text{NH}_3 + 5\text{O}_2$ | \rightarrow | $4\text{NO} + 6\text{H}_2\text{O}$ | (deep oxidation) |
| $4\text{NH}_3 + 7\text{O}_2$ | \rightarrow | $4\text{NO}_2 + 6\text{H}_2\text{O}$ | (deep oxidation) |
| 4. Undesirable degradation | | | |
| $\text{NH}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$ | \rightarrow | $\text{NH}_4(\text{HSO}_4)$ | |
| $2\text{NH}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$ | \rightarrow | $(\text{NH}_4)_2\text{SO}_4$ | |
| $2\text{NH}_3 + 2\text{NO}_2$ | \rightarrow | $\text{NH}_4\text{NO}_3 + \text{N}_2 + \text{H}_2\text{O}$ | |
| $(\text{NH}_2)_2\text{C}=\text{O}$ | \rightarrow | Polymeric products | |
| $\text{HNCO} + 3\text{NH}_3$ | \rightarrow | melamine ($\text{C}_3\text{N}_6\text{H}_6$) _x | |

2.3.4 Other Methods

2.3.4.1 *Plasma Techniques*

There are investigations to reduce NO_x emissions by a non-thermal plasma (NTP) in the gas phase. High energetic electrons usually generated in a corona discharge or dielectric barrier discharge react with the molecules in gas phase producing reactive species (radicals, excited molecules), which undergo further reactions. Recently, interesting results have been obtained from the combination of the gas-phase plasma reactions and the reaction of reducing agents on appropriate catalysts. It has been observed that an NTP in an oxygen-containing gas results in an effective oxidation of NO to NO_2 (Bröer and Hammer, 2000; Francke *et al.*, 2000; Kim *et al.*, 2001), which seems to be an essential intermediate step in the SCR reaction. The other effect of plasma is to partially oxidize hydrocarbons such as aldehydes. The formations of NO_2 and partial oxidized hydrocarbons are an important for NO_x reduction performance of the plasma-catalyst systems. It can take an advantage from using a plasma to develop a new class of catalysts that are potentially more durable, more active, more selective and more sulfur-tolerant compared to conventional lean- NO_x catalysts.

2.3.4.2 *NO_x Storage and Reduction (NSR)*

It was discovered that NO_x emission could be reduced more when the mass ratio of fuel to air (A/F) in the combustion conditions were alternated between the normal stoichiometric ratio and the lean-burn ratio in comparison to the steady lean-burn conditions. This concept is undertaken for the NO_x reduction under a two-stage operation instead of a single stage operation at a fixed air to fuel ratio. During a fuel-lean stage, NO_x is trapped on an adsorbent in nitrate form (NO_3^-). The excess oxygen present in this stage oxidizes NO to NO_2 over Pt site. It is subsequently stored on the barium oxide as barium nitrate. At the same time, hydrocarbons, H_2 and CO are readily oxidized into H_2O and CO_2 in this stage. When the engine is switched to fuel-rich stage at the normal air/fuel ratio, the exhaust is in oxygen deficient condition and hydrocarbons, H_2 and CO remain un-oxidized. Hence, these reductants react with the NO_3^- stored in the catalyst into harmless N_2 , H_2O and CO_2 . These processes are illustrated by Matsumoto (1996) and Misono and Inui (1999) as shown in Figure 2.4.

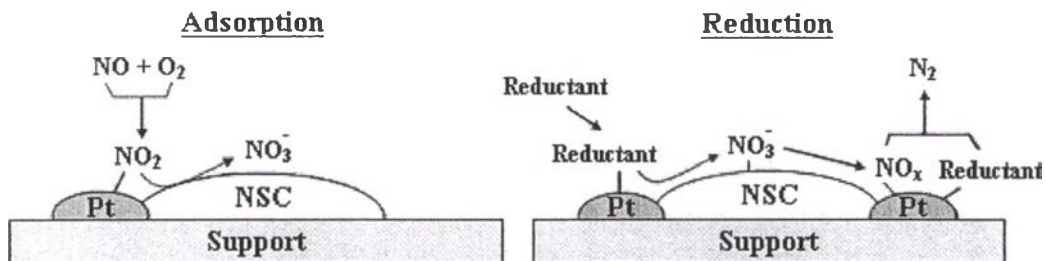


Figure 2.4 Adsorption and reduction of NO_x by NSR (NO_x storage and reduction) concept. NSC: NO_x storage compound (Gómez-García *et al.*, 2005).

The NO_x storage and reduction method was developed and commercialized by Toyota researchers (Matsumoto *et al.*, 1996; Takahashi *et al.*, 1996; Takeuch and Matumoto, 2004) for NO_x emission control under lean-burn conditions. NO_x storage materials consist of alkaline-earth or alkaline metals and noble metal like platinum or rhodium dispersed on the support such as alumina. The basicity of the storage component determines the amount of NO_x adsorbed. A main problem of sulfur poisoning in NSR catalysts is still challenge to overcome. SO₂ reacts with alumina to form aluminum sulfate which hinders the catalytic reactivity and it also competes with NO_x for BaO to form barium sulfate.

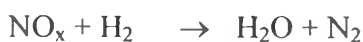
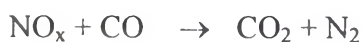
2.3.4.3 Non-selective Catalytic Reduction (NSCR)

This technique derived from automotive catalysis. Pt/Rh is the typical catalyst. Most of the commercial installations use either ceramic or metallic honey comb supports. The basic reactions chemistry occurs as follows (Heck, 1999):

Deplete oxygen:



Convert NO_x:



This technology applied in stationary source emission such as nitric plants. Life time of catalysts is expected ~10 years. Major catalytic deactivation occurs from ash deposit in the lubricating oil compared to minor case from thermal sintering.

2.3.4.4 Ozone Injection

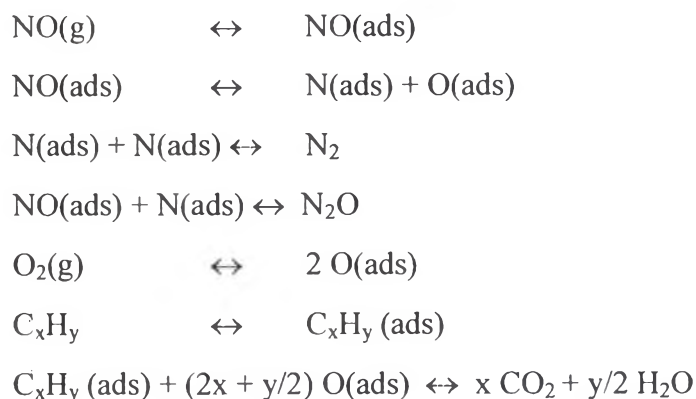
Ozone injection is an attractive technology as it is more energy efficient than plasma and electron beam processes. In this technique, small amount of oxygen or air can be discharged to produce ozone, which then is injected into the flue gas in order to convert NO to NO₂ via oxidation (Fu and Diwekar, 2004; Mok and Lee, 2006). The mixture of NO and NO₂ is further reduced to N₂ in a catalytic reactor. This method was very efficient to oxidize NO to NO₂ over a wide range of temperatures. The increase NO₂ content remarkably improved the catalytic reduction to nitrogen (Mok, 2004).

2.4 Mechanism of Selective Catalytic Reduction of NO_x

The mechanism of selective catalytic reduction of NO_x by hydrocarbons can be classified into 2 categories as described below.

2.4.1 Adsorption/Dissociation Mechanism

This approach involves the adsorption of NO on the active metal sites and subsequently dissociate into atomic N and O adsorbed on the surface. Then the adsorbed O is removed by reacting with hydrocarbon to form CO₂ while two adsorbed N combines to produce N₂. Non-dissociated NO also combines with adsorbed N to form N₂O. This mechanism is usually regarded on noble metal and Cu-ZSM-5 catalysts (Burch and Scire, 1994; Burch and Watling, 1997). The chemical state of the active site is very important in this mechanism. The previous research showed that Pt⁰ or Cu⁺ is active for NO dissociation (Fritz and Pitchon, 1997; Burch *et al*, 2002). The reducing agent has the important role to remove adsorbed O produced by dissociation of NO and O₂ from the catalytic surface and keep the active sites in a reduced state (Pt⁰ or Cu⁺). The main reactions of this mechanism are summarized as follows (Burch, 2004):



2.4.2 Oxidation-Reduction Mechanism

In this mechanism, several key intermediates are formed under the reaction conditions which are nitrates and nitrites, cyanides and isocyanates, carboxylates and acetates, and organo-nitrogen species. The similarity to type of intermediates has been detected on oxides and zeolites. However, it was unclear that such species are true intermediates or merely spectator species in the NO_x reduction reaction. The mechanism can be described in Figure 2.5 as shown.

The NO reacted with oxygen to produce some initial reactive intermediates such as NO_2 and NO_3 in the adsorbed form. Simultaneously, hydrocarbon was activated to hydrocarbon oxygenate. Over $\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst, acetate is regarded as reactive intermediates while formate is believed to be a spectator (Haneda *et al.*, 2003). Over $\text{Ag/Al}_2\text{O}_3$ and $\text{Sn/Al}_2\text{O}_3$ catalysts, acetate reacted actively with surface nitrates to form organo-nitrogen species which further hydrolyzed to form NCO, CN, and NH_3 (Shimizu *et al.*, 1999; Lee *et al.*, 2001). These hydrolyzed species then reacted with the surface nitrates or NO_2/NO to form N_2 . Most of the reaction mechanisms on metal oxide catalysts are consistent with this scheme. Bell *et al.* (Lobree *et al.*, 1997, 1998, 1999) reported that over Co-, Mn-, Fe- and Pd-ZSM-5 catalysts, the active intermediates were CN species. They reacted with NO_2 to form N_2 and CO_2 .

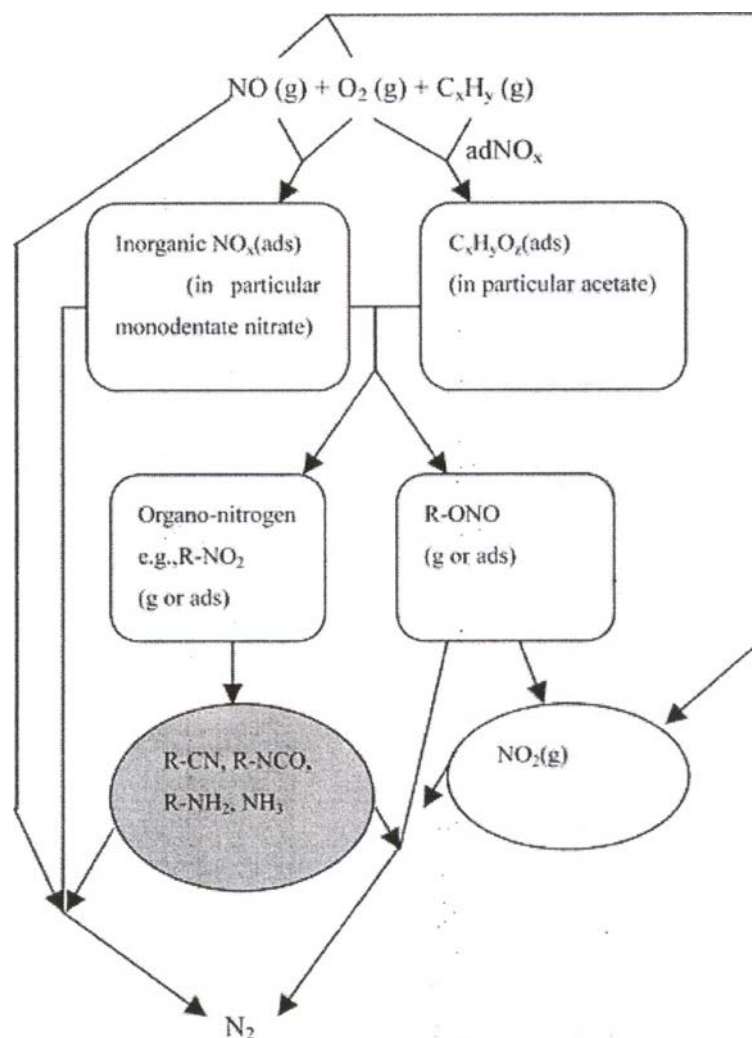


Figure 2.5 Reaction scheme of the oxidation-reduction mechanism (Meunier *et al.*, 2000).

It can be seen that the presence of oxygen shows positive effects in activating NO and hydrocarbon and oxidizing NO to more reactive NO_2 , which then reacts quickly with other intermediates such as R-NCO to form N_2 . The fact that replacing the reactant gas NO with NO_2 significantly improves the conversion of NO_x has proved that NO_2 plays an important role in the reaction process. However, oxygen also shows negative effects. At high temperatures, the unselective combustion of reductant becomes much faster than SCR leading to decreasing in the

amount of reductant remained for the SCR process. This results in the decline of NO_x reduction activity at high temperature regions. Consequently, the activity curve of HC-SCR exhibits a typical volcano shape. An example of the configuration of this curve is shown in Figure 2.6 as below. It describes the activities of Rh and/or Au catalysts prepared from impregnation (IMP) and ultrasound-assisted membrane reduction (UAMR) method.

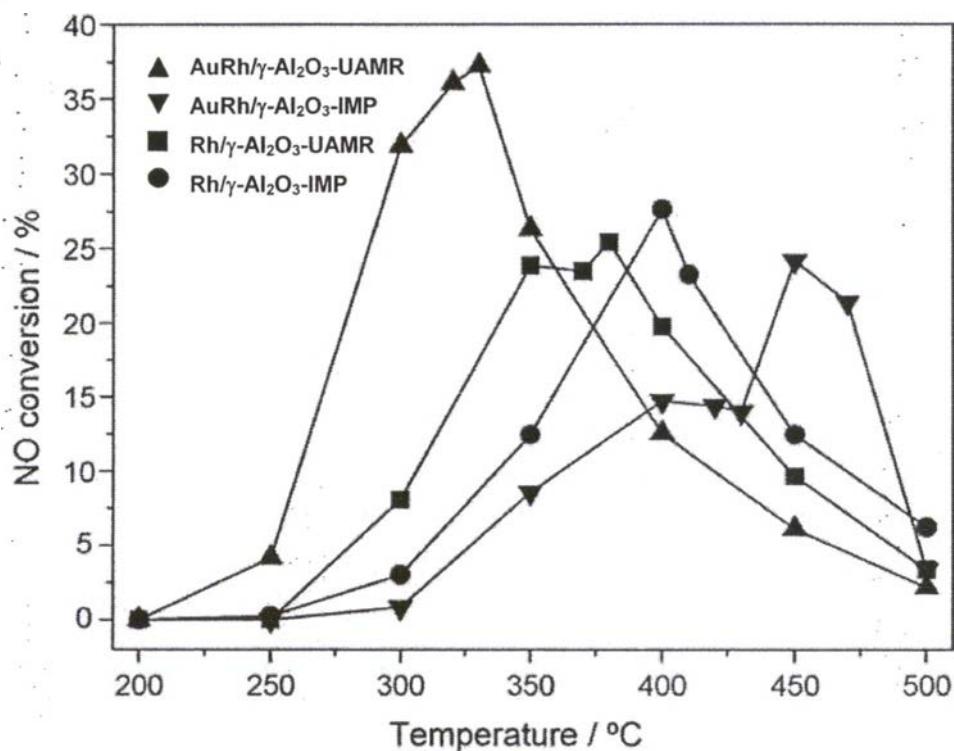


Figure 2.6 NO conversion curves of selective reduction with propene over supported Au and/or Rh on alumina catalysts (Liu *et al.*, 2009).