CHAPTER II

LITERATURE SURVEY

There are many attempts to alleviate the emission of NO_x both from stationary (power plants and chemical operations) and automotive (fuel combustion in diesel or lean-burn gasoline engines) sources.

Several technologies, which have been developed in recent years, can be classified according to their use or non-use of a catalyst. Non-catalytic technologies focus on improving combustion and cleaning of the fuels and will not be discussed in this thesis. Possible catalytic candidates for the further developments of this very necessary technology are described in more detailed as followed.

2.1 Catalytic Approach to NO_x De-Pollution

A large number of catalysts have been tested to eliminate NO through different reactions. It is possible to divide them into four groups.

2.1.1 The Catalytic Decomposition of NO

The direct decomposition of NO, which is a goal worth striving for since it eliminates the need for reductants, which in turn eventually eliminate the additional pollution associated with the other catalytic reduction methods.

Most attempts to develop practical decomposition catalysts have dealt with noble metals and metal oxides. Some of these materials are active in the reduced state, but oxygen contained in the feed gas or released by the decomposition of NO competes with NO for the adsorption sites and poisons the activity. To remove surface oxygen and regenerate catalytic activity, high reaction temperature and/or gaseous reductants are required. Copper ion-exchanged ZSM-5 zeolite and other cation-exchanged zeolites have been shown to be active for direct decomposition of nitric oxide to nitrogen and oxygen, however, their steady-state activities are markedly depressed in the presence of oxygen. (Iwamoto and Hamada, 1991).

2.1.2 The Selective Catalytic Reduction of NO with Ammonia

The selective catalytic reduction (SCR) with NH_i (ammonia, urea, etc.) in lean conditions was applied to reduce NO_x. However, it is not practical and safe in mobile applications (automotive vehicles) to use nitrogen containing reductants, which need a storage tank and an accurate control system to avoid toxic slip. Therefore, this technology can only be conveniently used on stationary sources, typical of chemical industrial plants and power stations (Hamada *et al.*, 1998)

2.1.3 The Catalytic Reduction of NO in the Presence of CO and/or H_2

The three-way automotive catalyst has been highly successful in controlling exhaust emissions from conventional petrol engines which operate close to stoichiometric conditions. However, the exhaust from lean-burn engines and from diesel engines contain over 5% oxygen. Under these conditions the three-way catalysts are no longer effective for NO_x control although they are still highly effective for carbon monoxide and hydrocarbon oxidation. For these automotive uses alternative catalytic systems must be developed (Burch *et al.*, 1994).

2.1.4 The Selective Catalytic Reduction of NO with Hydrocarbons

The selective catalytic reduction of NO in the presence of hydrocarbons (HC-SCR of NO) is a method that has not yet reached industrial use but can be applied both for automotive pollution control and in various industrial plants (Parvulescu *et al.*, 1998). In contrast to direct decomposition of NO, the presence of oxygen was found not to inhibit but promote NO reduction with hydrocarbon, a favorable feature for the reduction of NO in oxygen-rich exhaust gases.

For the HC-SCR of NO, the reducing gases have been classified into two groups, selective reductants: ethylene, propene, butene, and propane and non-selective reductants such as hydrogen, carbon monoxide, methane, and ethane.

The discovery of this interesting reaction was performed first in 1990, Held *et al.* (1990) and Iwamoto *et al.* (1991) showed independently that the catalytic activity of Cu-ZSM-5 could be greatly enhanced in an excess of oxygen by the presence of small amounts of hydrocarbons like ethylene and propene. Soon afterwards H-form zeolites, acidic metal oxides, and alumina-supported metals were also found to be effective (Hamada *et al.* 1990). Unfortunately, most of these catalysts are quite susceptible to interference caused by water vapor.

Iwamoto *et al.* (1991) reported that copper, cobalt, or iron is effective to enhance the catalytic activity of alumina for the selective reduction of NO with ethene in an oxidizing atmosphere. The addition of copper resulted in lowering the active temperature region, higher maximum activity, and the enhancement of the reaction rate. The maximum effect was observed at 0.3 wt % of the copper loading. They concluded that copper is classified to be an excellent additive to improve the catalytic activity of Al_2O_3 at temperature as low as 300-500 °C.

From a practical point of view, it is important to develop catalysts which are active in the presence of water since exhaust gases from lean-burn gasoline engines and diesel engines always contain water. This catalyst should operate under a large excess oxygen in the range of 2 to 10 vol% and moisture in the range of 10 to 15 vol%, at a large hourly space velocities over 1×10^{-5} per hour and in a wide temperature range of 400 to 1,000 K.

Miyadera (1993) investigated the effect of moisture on the selective reduction of NO with C_3H_6 over several alumina-supported metal catalysts. All catalysts prepared by impregnation method. He found that alumina-supported silver catalysts exhibited high activities in the presence of excess oxygen and water whereas moisture dramatically decreased the activities of Al_2O_3 and Co/Al_2O_3 which were highly active in the absence of water. The maximum activity of Ag/Al_2O_3 obtained at 2.0 wt % of Ag.

Bethke and Kung (1997) reported that the 2.0 wt % Ag/Al_2O_3 catalyst was much more effective at lean NO_x reduction with C_3H_6 than 6 wt % Ag/Al_2O_3. This difference was attributed to the Ag in the catalysts having different oxidation states under reaction conditions. The 2 wt % Ag/Al_2O_3 catalyst was in the oxidized form under all reaction conditions, while 6 wt % Ag/Al_2O_3 catalyst contained a large number of silver particle at lower temperature and less at high temperatures. The presence of silver leaded to a high rate of C_3H_6 combustion at the expense of N_2 formation.

Hoost *et al.* (1997) studied the activities of the Ag supported on a non-porous γ-Al_2O_3 in lean NO_x reduction with C_3H_6. The optimum Ag loading was 2 wt %. The results confirmed that Ag was primarily in an oxidized state during reaction.

It is suggested that the selective reduction of NO with hydrocarbons under oxygen-rich or lean conditions proceeds via a series of sequential and/or parallel reaction steps, probably catalyzed by different catalytically active species. Most researchers propose reaction mechanisms in which some kind of intermediates, such as NO_2, partially oxidized hydrocarbons, carbonaceous materials, and nitrogen-containing compounds leading to the formation of N_2, are formed during the reaction pathway. It is expected from the reaction mechanism that adequate combinations of catalytic species may give high-performance catalysts. (Hamada, 1997).

Burch *et al.* (1994) presented an extensive mechanistic study of supported platinum catalysts on γ-alumina for the selective reduction of NO in the presence of excess oxygen. The catalysts tested were prepared by incipient wetness impregnation method. This paper details a range of experiments, both conventional microreactor tests and TAP (Temporal analysis of products) studies, aimed at establishing the mechanism of the lean NO_x reaction over platinum-based catalysts. The results indicated that the predominant mechanism comprises two basic steps: reduction of the platinum sites by the hydrocarbon, followed by the decomposition of NO over these reduced platinum sites to generate N_2 and adsorbed O_2.

Hamada *et al.* (1996 a) demonstrated the cooperative function of Pt and alumina for Pt/Al_2O_3 by using a mechanical mixture of Pt/SiO_2 and Al_2O_3.

Jen (1998) investigated the reduction of NO over Ag/Al_2O_3 catalyst, which obtained by the wetness-incipient impregnation method. Under simulated exhaust conditions, Ag/Al_2O_3 showed a good activity for lean NO_x reduction. The activity increased as the O_2 concentration increased from 1.5 % to 10 % vol. The reactivity of the Ag-catalyst for the NO_x reduction was closely related to the activity for hydrocarbon-oxidation. The activity of the Ag/Al_2O_3 catalyst increased as the concentration of hydrocarbon increased and the space velocity of the gas mixture decreased. Moisture and SO_2 poisoned the activity of this catalyst for lean NO_x reduction.

Based on the one of the proposed reaction mechanisms, where the oxidation of NO is dominant, NO is first oxidizing to NO_2 with oxygen and then the resulting NO_2 reacts with hydrocarbons to form an active intermediate for the formation of N_2. There are many research works concentrated on this concept.

Hamada *et al.* (1996 b) investigated the promoting effect of supported metals on alumina catalyst for the reduction of NO in oxygen-rich atmosphere. For NO reduction with C_3H_6 over impregnated CoO/Al_2O_3, the first reaction step was found to be the oxidation of NO to NO_2 probably catalyzed by dispersed cobalt species. The next reaction step, which is the reaction of NO_2 with C_3H_6 to form N_2, was considered to take place on the alumina surface.

Ueda *et al.* (1997) studied the reduction of NO with propylene in the presence of oxygen and moisture over gold supported on several metal oxides. The catalysts were prepared by deposition precipitation and coprecipitation methods. They found that the reaction temperature varied depending on the kind of metal oxide support and increasing in the order of α-Fe_2O_3 ~ ZnO < MgO ~ TiO_2 < Al_2O_3. The highest conversion to nitrogen (about 70 %) was obtained over Au/Al_2O_3 with a metal loading of 0.1 to 0.2 wt % at 430 °C. The optimum ratio of C_3H_6 to NO concentration closed to the unity.

The effect of moisture on NO reduction with propylene presented a remarkable contrast between Au/Al_2O_3 and Al_2O_3. The conversion of NO to N_2 over Au/Al_2O_3 was not reduced, but slightly increased by the presence of water, although over Al_2O_3 alone it was markedly depressed. The amount of O_2 enhance the reduction of NO by C_3H_6 and NO_2 reacted C_3H_6 with at lower temperature than NO specifying that NO reduction could take place through the oxidation of NO to NO_2, which then reacted with C_3H_6.

Ueda and Haruta (1998) reported that Au/Al_2O_3 showed excellent activity for the selective reduction of NO with propene. This catalyst is characterized by its high resistance to moisture. After they found that the first reaction step was the oxidation of NO to NO_2, they tried to promote the activity of Au/Al_2O_3 by adding Mn_2O_3. It was discovered that the mechanical mixture of Au/Al_2O_3 with Mn_2O_3 catalyst was markedly active for the reduction of NO with propene, even in the presence of oxygen and moisture at temperature of 523 to 733 K.

However, one of the most important problems in these systems is that the oxidation catalyst or site for NO is frequently active for oxidation of the hydrocarbons, which would result in decrease in efficiency of the reductant.

Normally, the diesel exhausts contain very small amounts of unburned hydrocarbons though the concentration of NO is rather high. The addition of hydrocarbons or fuels into the diesel exhausts is necessary to reduce NO through the SCR-HC method.

From the basis of the above reaction mechanism and the essentiality of hydrocarbons addition, the novel strategy to reduce NO selectively was proposed by Iwamoto's group: intermediate addition of a reductant into the NO containing exhaust between an oxidation catalyst of NO to NO_2 and a reduction catalyst to N_2 or IAR method (Iwamoto *et al.*, 1998).

They studied $NO-C_2H_4-O_2$ by using a two-stage reactor, of which the first stage contains a NO oxidation catalysts and the second stage, a catalyst for the reaction between NO_2 and C_2H_4. The introduction of C_2H_4 between the two stages improved the efficiency of hydrocarbon utilization.

Beside, hydrocarbons oxygen-containing organic compounds such as methanol (Chadwick and Masters, 1998), ethanol (Miyadera, 1997), propanol (Haneda, *et al.* 1997), etc. were also effective in reducing nitric oxide over alumina and Cu-ZSM-5 catalyst in the presence of water and excess oxygen. Nevertheless, a large methanol/NO_x ratio is required to remove sufficient amount of NO_x with this process.

2.2 Sol-Gel Technology Applied in NO_x Removal

2.2.1 The Advantages of Sol-Gel Method

The process for the formation of solids from gel is called sol-gel method. One of the features of this method is the formation of liquid phase precursors consisting of M_1-O-M_2 bonding during mixing the metal alkoxides dissolved in the organic solvent, where M_1 is the host metal ions and M_2 the doped and/or mixed metal ions. Thus the homogeneous distributions of metal ions are expected in the gels prepared by hydrolysis of the liquid phase precursors and, consequently, in the dried powders. High purity of the products is also the great feature of sol-gel method. Therefore, it has often been applied to the preparation of catalysts in order to avoid some inconveniences derived from impurities in the catalysts (Ueno, 1992).

Since catalytic reactions take place on the surface of metal particles in a supported metal catalyst. Not only the activities but also the product selectivity are improved on small sized metal particles. The sol-gel method is one of the promising techniques to control metal particle sizes in the supported metal catalysts (Ueno, 1992). The control of pore size is significant, as suggested by the theoretical modeling of Ruckenstein and Pulvermacher, because the rate of sintering can be reduced when the size of the metal particle is matched to the size of the pore. This model assumes that metal particle growth occurs as a result of surface diffusion (Gonzalez *et al.*, 1997).

One can tailor make catalyst to fit particular applications by using this method. Other advantages include higher BET surface area, improved thermal stability of the supported metals, well-defined pore sizes distributions, and the ease with which additional elements can be added (Gonzalez and Lambert, 1997).

2.2.2 The Preparation of Supported Metal Sol-Gel Catalyst

According to the synthesis of sol-gel, it occurs in two distinct steps as following (Gonzalez *et al.*, 1997):

1. Pregelation, which occur when the reactants (alkoxides and metal precursors) hydrolyze and condense to form a gel.

The hydrolysis can be obtained as followed, when metal alkoxide reacts with water to form hydroxyl group of metal.

$$(RO)_m\text{-}M + H\text{-}O\text{-}H \longrightarrow (RO)_{m-1}\text{-}M\text{-}OH + R\text{-}OH \qquad (2.1)$$

Where

M = metal corresponding to the alkoxide
m = metal valence
R = alkyl group (CH_3, C_2H_5, C_3H_7, etc.)

After that, the condensation or polymerization can be achieved when alkoxide groups (M-OR) react with hydroxyl groups (M-OH) formed during the hydrolysis to form metaloxanes (M-O-M). The reactions that take place are as given below.

$$\equiv M\text{-}OH + HO\text{-}M\text{-}\equiv \longrightarrow \equiv M\text{-}O\text{-}M\equiv + HOH \qquad (2.2)$$

$$\equiv M\text{-}OR + HO\text{-}M\text{-}\equiv \longrightarrow \equiv M\text{-}O\text{-}M\equiv + ROH \qquad (2.3)$$

2. Postgelation, the second stage in the sol gel synthesis, changes that occur during the drying and calcination of the gel include the desorption of water, the evaporation of the solvent, the desorption of organic residues, and the dehydroxylation reactions and structural changes.

The evaporation of the solvent during drying leads to the formation of strong capillary forces. These capillary forces arise from the difference between solid-vapor and solid-liquid interfacial energies.

There are many variables, which influence the sol-gel product such as water/alkoxide ratio, reaction pH, the influence of the solvent, time, temperature of reaction, the different alkyl groups, and the metallic precursor used.

2.2.3 Sol-Gel Research Work Applied in No_x Removal

Hamada *et al.* (1997) studied the effect of cobalt ion dispersion upon the selective catalytic reduction of NO by propene on CoO/Al_2O_3 catalysts. They concluded that highly dispersed cobalt ions in the sol-gel catalysts were ready to react with alumina to form cobalt aluminate ($CoAl_2O_4$) by calcination at 773 K, and exhibited a high activity for SCR-NO. While in the impregnated catalysts $CoAl_2O_4$ crystallites were not formed by calcination at 773 K, which resulted in the poor activity, because of the poor dispersion of cobalt ions in the catalyst. The most important factor for the preparation of CoO/Al_2O_3 catalyst to be employed for SCR-NO is in the dispersion states of Co ions.

Kung *et al.* (1997) reported the activity of Co/Al_2O_3 catalyst for the selective catalytic reduction of NO_x by propene or propane. Al_2O_3 support was prepared by sol-gel method using aluminum isopropoxide, 2-methhylpentane-2,4-diol, and isopropanol as the starting materials. Then the Co/Al_2O_3 catalyst was obtained by impregnating the sol-gel Al_2O_3 with a $Co(NO_3)_2$ precursor followed by a 800 °C calcination.

The characterization of the catalysts with UV-vis spectroscopy, temperature-programmed reduction by H_2, XRD, iodometric titration, and BET surface area measurements led to the proposal that there exist four different Co species: Co^{2+} ions in $CoAl_2O_4$, small Co_3O_4 clusters that interact strongly with

Al_2O_3, large Co_3O_4 particles, and dispersed surface Co^{2+} ions in octahedral coordination. The latter Co^{2+} species were responsible for the SCR activity. In contrast, particles or surface clusters of Co_3O_4 only catalyze the nonproductive combustion of hydrocarbons, and the Co^{2+} ions in $CoAl_2O_4$ were inactive.

Castillo *et al.* (1998) presented the synthesis of Pt and Rh catalysts supported on alumina and titania using the sol-gel method in order to understand the influence of the preparation method on the reduction of NO with CO. In sol-gel catalysts, a redispersion of the metal phase and higher resistance to sintering was observed. On the other hand, in the impregnated catalyst, a sintering effect was observed. The sol-gel catalyst showed higher activity than that of impregnated reference catalyst, mainly when titania is the support. Moreover, sol-gel preparations are more selective to N_2, whereas impregnated reference catalysts are selective to N_2O. The increase in dispersion and high resistance to sintering on sol-gel catalysts was interpreted as a surface migration effect of the metal particles buried in alumina and titania gels.

Hamada *et al.* (1998) investigated the reduction of NO by various light hydrocarbons on sol-gel alumina based indium (In), galium (Ga), tin (Sn), silver (Ag), and cobalt (Co) catalysts. A remarkable enhancement was achieved by using sol-gel alumina instead of conventional γ-alumina as a support or a catalyst. Sol-gel alumina based catalysts showed a promising resistance against the deactivation caused by water. They also found that the supported alumina prepared by a sol-gel method had high surface area and accordingly active alumina sites for the reaction.

Moreover, the promotive effect of manganese oxide additives on NO reduction activity was also investigated over several alumina based In and Ga catalysts.

Gulari and Seker (1998) presented results, which demonstrate that a 1 % Pt/alumina catalyst prepared by the single step sol-gel technique was greater in its N_2 selectivity in the catalytic reduction of NO_x by propene. This result was compared with similarly loaded Pt/alumina catalyst prepared by the more commonly used impregnation technique.

The selectivity of the sol-gel catalyst to N_2 at maximum conversion was 83 % as compared to 43 % and 60 % selectivity observed with Pt catalysts prepared by impregnation technique. According to the resistance to water, the sol-gel made catalyst did not change its activity and selectivity in the presence of 2.5 % moisture.

Kung *et al.* (1999) reported the catalytic properties of highly active $Sn/\gamma\text{-}Al_2O_3$ for lean NO_x reduction. The $Sn/\gamma\text{-}Al_2O_3$ was prepared by incipient wetness impregnating the solution of $SnCl_2$ on $\gamma\text{-}Al_2O_3$ which prepared from the hydrolysis of aluminum isopropoxide in 2-methylpentane-2, 4-diol. They concluded that the $Sn/\gamma\text{-}Al_2O_3$ is effective NOx reduction catalyst. Although the nature of the active sites is not yet known at present, these catalysts showed stable, high activities above 400 °C, even at high partial pressure of O_2 and H_2O. This temperature range would be suitable for treatment of exhaust from heavy duty diesel engines.