CHAPTER II
LITERATURE SURVEY

The role of catalysis in environmental improvement is crucial. The concepts for developing catalysts for environmental catalysis are quite different from those for the conventional petrochemical catalysis. Because petrochemical catalysts can use purified raw materials and apply the best reaction conditions for the production of objective materials. In contrast, environmental catalysts have to work under very severe conditions; very wide temperature range, high space velocity, low concentration of target materials, very high concentration of co-existing gases and poisons, and great change of the reaction conditions. Therefore the environmental catalysts must have high activity, selectivity, and durability.

2.1 The Selective Catalytic Reduction of NO_x over Ag/Al_2O_3 Catalyst

Miyadera (1993) studied the selective catalytic reduction of NO with propylene (C_3H_6) and oxygen containing organic compounds over several alumina-supported metal catalyst they found that Ag/Al_2O_3 catalyst showed high activity in the presence of water and excess oxygen, while the activity of Al_2O_3 and Co/Al_2O_3 catalyst decreased significantly in the presence of water. It is also found that oxygen containing organic compounds such as ethanol and acetone were more effective than propylene in reducing nitric oxide over Ag/Al_2O_3 catalyst in the presence of water and excess oxygen.

Bethke and Kung (1997) studied the activities of 2 and 6 wt% Ag/Al_2O_3 catalysts for lean NO reduction with C_3H_6. They found that the 2 wt% Ag/Al_2O_3 catalyst is much more effective at lean NO_x reduction than the 6 wt% Ag/Al_2O_3. This difference is attributed to the Ag in the catalysts having different oxidation states under reaction conditions. The 2 wt% Ag/Al_2O_3

catalyst is in the oxidized form under all reaction conditions, while the 6 wt% Ag/Al_2O_3 catalyst contains a large number of Ag^0 particles at lower temperatures and less at higher temperatures. The presence of Ag^0 leads to a high rate of C_3H_6 combustion at the expense of N_2 formation.

Hoost *et al.* (1997) studied the activities of Ag supported on a nonporous γ-Al_2O_3 in lean-NO_x reduction. The optimal metal loading was 2 wt%. The 2 wt% Ag/Al_2O_3 catalyst prepared by multiple impregnation was more active for lean-NO_x reduction than prepared by using a single impregnation step.

Takagi *et al.* (1998) studied the selective catalytic reduction of NO on Ag/Al_2O_3 catalysts prepared from bohemite needles. Ag/Al_2O_3 catalysts showed good performances especially when ethanol is employed as a reducing agent in the presence of water. Temperature programmed reduction (TPR) study revealed that the Ag species strongly interact with the alumina surface and the oxidized Ag species contribute positively for the improvement of the catalytic activity at temperatures above 750 K.

Jen (1998) studied the reduction of NO over Ag/Al_2O_3 catalysts with C_3H_6 or C_3H_6/C_3H_8 mixture in excess oxygen. The activity for NO-reduction increased as the oxygen-content in reaction mixture increase from 1.5% to 10%. The reactivity of the Ag-catalyst for the NO_x -reduction was closely related to the activity for hydrocarbon oxidation. The activity of Ag/Al_2O_3 catalyst increased as the concentration of hydrocarbon increased and the space velocity of the gas mixture decreased. The presence of water and SO_2 poisoned the activity of a Ag/Al_2O_3 catalyst for lean-NO_x reduction.

Seker *et al.* (1999) studied the selective catalytic reduction of NO over Ag/Al_2O_3 catalysts by propylene in the presence of oxygen. Ag/Al_2O_3 catalyst prepared by co-precipitation, impregnation, and single step sol-gel methods. The catalysts prepared by the sol-gel method were found to be the most active catalysts for selective reduction of NO_x with almost 100% selectivity to N_2.

Increased silver loading resulted in a catalyst that was more active at higher space velocities and had a broader activity window. The sol-gel catalysts also had better performance in the presence of water vapor.

Meunier *et al.* (1999) studied the selective catalytic reduction of NO with propylene in the presence of oxygen by using γ-Al_2O_3, 1.2% Ag/γ-Al_2O_3, and 10% Ag/γ-Al_2O_3 catalysts. The γ-Al_2O_3 and the low-loading silver material exhibited high conversions to N_2 whereas the high-loading sample predominantly yield N_2O.

Keshavaraja *et al.* (2000) studied the selective catalytic reduction of NO with methane over Ag/Al_2O_3 catalyst prepared by a single-step co-gelation technique. This type catalyst is active over a wide-temperature range (450-650° C), and for a relatively wide range of Ag loading (1-7 wt%). Excess oxygen in the feed gas favors the selective catalytic reduction reaction. The catalyst activity/stability remained high under demanding reaction conditions, and high space velocities.

Meunier *et al.* (2000) studied the distribution of gaseous products and the nature of surface species generated during the selective catalytic reduction of NO with propylene in the presence of oxygen over both a 0.4% Co/γ-Al_2O_3, and a sulfated 1.2% Ag/γ-Al_2O_3 catalyst. High concentration of NO_2 were observed in the product stream of the SCR reaction over both catalysts. The result shows that the NO_2 was formed via an alternative route to the direct oxidation of NO with O_2. The yields of NO_2 were higher over the Co/γ-Al_2O_3 than over the other materials and in contrast to the other materials, no NH_3 was produced over the Co/γ-Al_2O_3 catalyst.

2.2 The Selective Catalytic Reduction of NO_x over Pt/Al_2O_3 Catalyst

Burch *et al.* (1994) studied the selective catalytic reduction of NO in the presence of a large excess of oxygen over Pt/Al_2O_3 catalysts. Under typical operation conditions, propylene is a far more efficient reductant than either CO or hydrogen. The catalysts are very active and selective for the reduction of NO by propylene as low as 200°C. They found that in the decomposition step it has been shown that oxygen from NO is retained on the surface of platinum and blocks the surface for further adsorption/reaction of NO reduction reaction.

Inanba *et al.* (1996) studied the selective catalytic reduction of NO with propylene in the presence of oxygen over Al_2O_3, Pt/Al_2O_3, Pt/TiO_2, and physical mixtures of Pt/SiO2 and Al_2O_3. They found that catalyzed NO reduction to N_2 happened only above 400°C, Pt/Al_2O_3 was active for NO reduction to N_2 and N_2O at about 300-400°C but Pt/SiO_2 did not show any $deNO_x$ activity. The activity of physical mixtures of Pt/SiO_2 and Al_2O_3 was similar to Pt/Al_2O_3. They conclude that the reduction of NO to N_2 and N_2O results from successive reaction step over platinum and alumina.

Robert and Amiridis (1997) studied the selective catalytic reduction of NO by propylene over a 0.8 wt% Pt/Al_2O_3 catalyst in the temperature range of 200-500°C. the results indicate the presence of 2 kinetically distinct regions at temperatures above and below the temperature of maximum NO reduction. A maximum in NO conversion occurs at the C_3H_6 light-off temperature. Nitrogen selectivities are significantly different in the 2 regions, and are primarily affected by the amount of C_3H_6 available for the NO- C_3H_6 reaction.

Cho *et al.* (1998) investigated the physical and chemical properties of Pt/Al_2O_3 prepared by sol-gel method. Its pore structure, metal dispersion, catalytic activity, and sintering resistivity were compared with those of impregnation catalysts. The $Pt/\gamma\text{-}Al_2O_3$ catalysts prepared by the addition of platinum precursor to the alumina sol had similar physical properties to the conventionally prepared impregnation catalyst, but the $Pt/\gamma\text{-}Al_2O_3$ catalysts prepared by sol-gel method show higher thermal stability of metal particles than the conventional impregnation catalyst.

Seker and Gulari (1998) found that it is possible to make a highly selective Pt/Al_2O_3 catalyst for the reduction of NO_x by propylene under oxidizing conditions by changing the preparation procedure. This new procedure narrows the temperature window on the low temperature side while increasing the selectivity dramatically. The addition of water widens the temperature window on the high temperature side without negatively affecting the conversion or selectivity.

Efthimiadis *et al.* (1998) studied the effect of CH_4, H_2O, and SO_2 on the NO reduction with propylene over Pt/Al_2O_3 catalyst. The presence of water in the feed gas stream caused a small, reversible, inhibition effect over the Pt/Al_2O_3 catalyst. The peak temperature was not affected by the addition of water to the feed gas stream. The presence of SO_2 in the feed gas stream did not affect the NO_x conversion over Pt/Al_2O_3 catalyst.

Captain and Amiridis (1999) investigated the selective catalytic reduction of NO by propylene over a 0.8 wt% Pt/Al_2O_3 catalyst by using in situ Fourier transform infrared (FTIR) spectroscopy. They found that NO adsorption resulted in the formation of nitrate species associated with the Al_2O_3, as well as surface NO species associated with Pt. Similarly C_3H_6 adsorption resulted in the formation carboxylate species associated with alumina as well as surface CO associated with Pt. Finally, experiments conducted with the reactive NO- C_3H_6-O_2 mixture resulted in the formation of surface cyanide (-CN) and isocyanate (-NCO) species.

Nikolopoulos *et al.* (1999) compared the activity of Pt/Al_2O_3 and Rh/Al_2O_3 catalysts which used for the selective catalytic reduction of NO with C_3H_6 in the presence of excess oxygen. They found that Pt/Al_2O_3 was more active for NO reduction at lower temperature compared to Rh/Al_2O_3.

Narula *et al.* (2000) studied the activity of Pt/Al_2O_3 and Pt/SiO_2-Al_2O_3 catalysts. They found that Pt supported on sol-gel processed SiO_2-Al_2O_3 materials exhibited enhanced deNO_x efficiency under lean conditions and improved durability when compared with Pt supported on γ-Al_2O_3. Then they tested by using a 2-stage catalyst of Rh/SiO_2-Al_2O_3 followed by Pt/SiO_2-Al_2O_3. They found that it was possible to widen the NO_x conversion window.

Denton *et al.* (2000) examined the influence of various parameters over a large range of initial metal dispersion: nature of the support (silica or alumina), nature of the platinum precursor salt, and Pt particle size distribution. They found that the Pt dispersion was a major factor affecting the intrinsic activity of the reactions, while the nature of the support (SiO_2 or Al_2O_3), the porosity and impurities of the support, and the nature of Pt precursor were less important and not easily discernible.

Seker and Gulari (2000) investigated the activity and N_2 selectivity of sol-gel prepared Pt/Al_2O_3 catalysts for selective NO_x reduction. They found that when compared to the impregnation catalysts, the sol-gel catalysts have superior N_2 selectivity both in terms of percentage of NO converted to N_2 and comparable activity. Both the value of the minimum selectivity and the NO_x conversion are functions of oxygen concentration in the feed.

2.3 The Selective Catalytic Reduction of NO_x over Ag/TiO_2 Catalyst

Armiridis *et al.* (1996) studied the effect of vanadia content on the activation energy of the selective catalytic reduction of NO by ammonia over V_2O_5/TiO_2, $V_2O_5/TiO_2/SiO_2$, and V_2O_5-WO_3/TiO_2, catalysts. They found a significant decrease in activation energy when the vanadia surface concentration is increased. They still found the same result from tests conducted in the presence and absence of water vapor and SO_2.

Haneda *et al.* (1998) studied the reaction mechanism of NO reduction by C_3H_6 over Ag/TiO_2-ZrO_2 catalyst by using in situ FT-IR combined with catalytic activity studies. They found that silver plays an important role as the active species. In situ FT-IR detected organic nitro (-NO_2), nitrite (-ONO), inorganic NO_3^-, carbonate, formate, and/or acetate when TiO_2-ZrO_2 and Ag/TiO_2-ZrO_2 were exposed to a gas mixture of $NO+C_3H_6+O_2$ at room temperature. Isocyanate species was observed by an intense IR band along with disappearance of -ONO and NO_3^- species on Ag/TiO_2-ZrO_2 by evacuation at the temperature above 300°C after the reaction of $NO+C_3H_6+O_2$. The reactivity of -NCO species was much higher than that of cyanide (-CN) species, and the -NCO band was detected on TiO_2-ZrO_2 under the dynamic condition. They concluded that the role of silver is to promote the formation and the reaction of -NCO species. N_2 was considered to be formed from -NCO and NO_2.

Kameoka *et al.* (1998) studied the role of organic nitro compound such as nitromethane and nitroethane in selective reduction of NO_x with ethanol over different supported silver catalysts (Ag/Al_2O_3, Ag/TiO_2, Ag/SiO_2) by using infrared spectroscopy. They found that catalyst support affect the N_2 formation in the selective catalytic reduction of NO_x on supported silver catalysts. They concluded that the efficiency of supported silver catalyst in NO_x reaction with ethanol may be correlated with the nature of NCO species such as stability, reactivity which was formed by the decomposition of organic nitro compounds.

Wang *et al.* (1999) synthesized nanometer sized Ag/TiO_2 by irradiation of an $AgNO_3$ solution containing colloidal TiO_2 with light of wavelength (λ) smaller than 330 nm. After they used TEM, they found that silver clusters produced by photochemical reduction are indeed on the surface of TiO_2 particles, and the silver clusters showed the properties of microcrystallites.

Lopez *et al.* (1999) prepared titania-magnesia (TiO_2-MgO) mixed oxides by using the sol-gel method with titanium n-butoxide and magnesium ethoxide as precursors. They characterized the mixed oxides with XRD, BET, ESR and by testing their catalytic activity for 2-propanol and 2-butanol dehydration. They found that the selectivity patterns of the mixed oxides did not correspond to a simple addition of those observed for pure TiO_2 and pure MgO, and the interaction between the different crystalline structures coexisting in the mixed oxide should be responsible for observed activity and selectivity patterns.

Escobar *et al.* (2000) studied the influence of the synthesis additive (HNO_3, NH_4OH, and CH_3COOH) on the textural and structural characterization of sol-gel Al_2O_3-TiO_2. They found that HNO_3-catalyzed sample showed lower surface area and pore volumes. TiO_2-rich samples showed higher surface areas than Al_2O_3-rich oxides, but at more severe conditions they suffered a severe specific area loss. The alumina-rich formulations showed good stability in the whole range of temperatures studied.

2.4 The Selective Catalytic Reduction of NO_x over Pt/TiO_2 Catalyst

Scheider *et al.* (1994) synthesized high surface area platinum-titania (Pt/TiO_2) aerogels by the sol-gel-aerogel method. They found that the Pt/TiO_2 aerogel have a BET surface area of 150 to 190 m^2g^{-1} and the titania matrix consists of anatase crystallites of about 8-9 nm mean size. All aerogel catalysts showed a stability of both the titania matrix and the platinum particle toward air or hydrogen at temperature up to 673 K. They compared a commercial Pt/Al_2O_3 catalysts to the Pt/TiO_2 catalysts, the untreated 2-5 wt% Pt/TiO_2 catalysts show a markedly high catalytic activity. They concluded that air pretreatment at 573 K or above had either no or promoting influence on activity. In contrast, pretreatments in hydrogen produced either no or detrimental activity change.

Castillo *et al.* (1998) synthesized platinum and rhodium supported on alumina and titania by the sol-gel method, then they characterized and tested the catalytic activity for the reduction of NO by CO_2. They compared the sol-gel catalysts to the impregnated catalysts. They found that the sol-gel catalysts showed higher activity than that of impregnated catalysts, mainly when the titania is the support, and the sol-gel catalysts are more selective to N_2, whereas impregnated catalysts are selective to N_2O.

Sanchez *et al.* (1996) prepared Pt/TiO_2 catalysts by sol-gel method. They characterized the crystalline structure by X-ray diffraction method. They found that all samples have three nanophases, composed of rutile (the majority phase), anatase and platinum. These samples were characterized by FTIR spectroscopy method. It showed that platinum promoted the formation of rutile, or the platinum-catalyzed dehydroxylation of anatase. They concluded that platinum atoms did not go into the crystalline structure of rutile although PtO_2 and rutile have the same crystalline structure.

Bahamonde *et al.* (1998) studied the lean-burn $deNO_x$ process by using Pt/TiO_2 catalysts. These catalysts were prepared with mixtures of titanium dioxide and a natural magnesium silicate. They found that the platinum solution concentration and impregnation times have a strong influence on the catalysts metal content. Platinum enhances the activity of titania and activity increased with increasing platinum content.

Blanco *et al.* (1998) studied the activity of titania based copper and platinum monolithic catalysts in the reduction of NO_x with exhaust gases from a diesel engine injecting fuel as the reductant. They combined both catalysts as a two-stage system. They found that two NO_x conversion maxima were observed with Pt/TiO_2 at 225°C and 350°C operating at 6.6 m s^{-1} and NO_x conversion were achieved in the temperature range 200-450°C.

Ingemar Odenbrand *et al.* (1998) studied the catalytic behavior of a copper and a platinum titania in the catalytic reduction of nitrogen oxides with hydrocarbons in real diesel conditions, therefore diesel fuel was the reductant. Both catalysts were active in the reduction reaction of these conditions. They found that the selectivity in the reduction of NO to NO_2 was relatively low with both titania supported systems.

Harizanov and Hrizanova (2000) studied a technological approach for the sol-gel processing of stabilized xerogel colloidal titanium oxide films, by using glycerol as a drying control additive agent. Glycerol was used for stabilizing the solution. They found that a nanocrystalline titania anatase film of high optical quality would be obtained by the sol-gel process.