

CHAPTER II

LITERATURE REVIEWS

The control of NO in the exhaust gases from automobiles equipped with gasoline engines has been successfully performed by the use of so-called three-way conversion system. As for NO_x generated from stationary sources, ammonia has been used as a reduction agent to advance the de-NO_x reaction on V₂O₅ /TiO₂. In this condition, the presence of O₂ does not hinder but accelerates the reaction. However, for de-NO_x from the exhaust gases of diesel engines or lean burn facilities, which involve a large excess of O₂, no practical catalyst systems have been developed, and intensive effort has been made to overcome this difficulty. Most recently, some studies on the NO decomposition and the selective reduction of NO by hydrocarbons in oxidizing atmosphere were reported using catalysts such as H-type zeolite, metal-ion-exchanged zeolites, and some metallosilicates [29]. Some of the more investigations and the evolution of these catalysts are summarized below.

Promotive effects of the addition of alkaline earth metals to Ce-ZSM-5 catalyst for nitric oxide reduction were investigated by Yokoyama and Misano [30]. They found that the addition of alkaline earth metals to Ce-exchanged ZSM-5 enhance remarkably the catalytic activity for the removal of nitric oxide in the presence of propane and oxygen. The activity was great even at the space velocity of 10,000 h⁻¹.

Ault and Ayen [31] found that the conversion data for the reaction of nitric oxide with C₁ to C₈ hydrocarbons over a barium-promoted copper chromite catalyst were obtained in an integral flow reactor operated at atmospheric pressure and temperatures of 225°- 525 °C. In general, an increase in carbon number in the hydrocarbon studied resulted in a decrease in the required temperature for a given nitric oxide conversion decreased with degree of saturation.

The zeolite supported PtRh catalysts for CO oxidation and NO reduction were studied by Tzou et al. [32]. PtRh bimetallic particles evidenced by EXAFS at Pt L₃-edge and Rh K-edge, were prepared in the supercages of NaY zeolites. Bimetallic catalysts, PtRh/NaY, were more reactive in CO-O₂ and CO-NO reaction than their corresponding monometallic catalysts, Pt/NaY and Rh/NaY.

Li and Armor [33] discovered a family of catalysts that can effectively reduce NO_x with methane in the presence of excess oxygen. This new catalytic chemistry offers an alternative means for controlling NO_x emissions. Complete reduction of nitric oxide was obtained at 400 °C over Co-ZSM-5 catalyst. The presence of oxygen in the feed greatly enhances the nitric oxide reduction activity on Co-ZSM-5, and the nitric oxide conversion is strongly related to the inlet methane level. On the other hand, Cu-ZSM-5, which is a unique catalyst for the direct nitric oxide decomposition, is poor catalyst for nitric oxide reduction by methane in the presence of excess oxygen.

Kicuchi et al. [34] studied reduction of nitric oxide with propane. They reported that gallium ion-exchanged zeolite catalysts, among which ferrierite(Ga-ferrierite) and ZSM-5 (Ga-ZSM-5) showed high activity in a wide range of reaction temperature.

Takita et al. [35] studied the selective reduction of nitric oxide with propane over Cu-silicoaluminophosphate(SAPO) under oxidizing atmosphere. They found that Cu-SAPO-34 exhibits higher activity for NO reduction than Cu-ZSM-5 and the high catalytic activity of Cu-SAPO-34 was sustained up 600 °C. Furthermore, heat resistance of Cu-SAPO-34 is superior to Cu-ZSM-5.

Iwamoto et al. [36] studied the NO reduction on iron ion-exchanged zeolite. They observed that among various metals ion-exchanged mordenite was the most active for the

selective reduction of NO to nitrogen by ethene in the presence of oxygen at the temperature as low as 473 K. The catalytic activities of iron ion-exchanged zeolite depended on the zeolite structure and the iron ion-exchange level. The effect of the zeolite structures are in the order of MOR > FER > MFI > Y > LTL at 473 K. The activity of iron ion-exchanged mordenite increased with the increment in the exchange level and leveled off above about 60 %.

Kikuchi et al. [37] reported that selective reduction of nitric oxide with propane in the presence of excess oxygen was investigated using gallium ion-exchanged zeolite catalysts. Gallium ion-exchanged ferrierite (Ga-ferrierite) showed extremely high selectivity for this reaction under oxygen-rich conditions(10%). The molar ratio of reacted NO to consumed C₃H₈ was found to be near 3 on Ga-ferrierite.

The selective reduction of nitric oxide with hydrocarbons over H-form zeolite catalysts in oxygen rich atmosphere were studied by Hamada et al. [38]. They suspected that the active centers of the zeolites for selective reduction are their acid sites based on the fact that activity of H-ZSM-5 is higher than Na-ZSM-5 or silicate and that silica gel is quite inactive.

Hamada et al. [39] studied selective reduction of nitric oxide with propane. They suggested that the oxidation of nitric oxide was oxidized to nitrogen dioxide intermediate which is reduced to nitrogen by reaction with propane. The direct oxidation of propane with oxygen is a side reaction. Probably the high selectivity of the reduction is caused by the higher reactivity of nitrogen dioxide to hydrocarbons than that of oxygen over alumina and H-ZSM-5, which are poor catalysts for the activation molecular oxygen. The decrease in nitric oxide conversion to nitrogen at high temperatures could be explained by the high rate of propane - oxygen reaction.

NO decomposition on copper - incorporated A-zeolites were observed by Inui et al. [40]. They found that copper containing A-type zeolites which contained copper with considerably high concentrations were synthesized through crystallization. It was confirmed that Cu^+ ions in the crystals could be stably maintained compared with those in copper-loaded samples prepared by an ion-exchanged method. NO decomposition activity on the Cu-A catalyst corresponded to the capacity of redox response. Even under an excess oxygen condition the NO decomposition progressed smoothly at around 300-350 °C by the addition of a very small concentration of n-C₈ - n-C₁₆ saturated hydrocarbons. Especially cetane(n-C₁₆) exhibited the marked effect, and NO was decomposed completely at that temperature range. Microscopic Sequential Reaction mechanism was proposed and the necessary conditions to realize this mechanism were discussed.

Kikuchi et al. [41] found that H-form Fe-silicate catalysts showed high activity and stability for the reduction of NO with propylene in the presence of a high concentration of oxygen. The catalytic activity of Fe-silicate was hardly affected by the presence of SO₂.

Inui et al. [29] studied the decomposition of nitric oxide on metallosilicates. Catalytic removal of NO was conducted under the condition of large excess O₂ by using difference kinds of metallosilicates having MFI structure. With in coexistence of low concentration of cetane, H-Fe-silicate, which had both acidity and redox property, exhibited the maximum performance among the catalysts tested at a fairly lower temperature range, around 350 °C, and the NO was totally converted. The temperature dependence of NO conversion was coexistently similar to that cetane combustion.

Zecchina et al. [42] found that an exchange procedure the acidic protons of H-ZSM-5 by Cu^I ions through reaction with CuCl in the gas phase. In the so obtained Cu^I-ZSM-5 exchanged zeolite the Cu^I ions are in well defined configuration and form with NO mono and di-nitrosyl complexes of high structural and spectroscopic quality. The Cu^I(NO)₂

species are transformed at room temperature into $\text{Cu}^{\text{II}}(\text{NO})\text{X}$ ($\text{X}=\text{O}^-$ and/or NO_2^-) species which could represent an intermediate in NO decomposition.

Inui et al. [43] studied the characteristic of some copper containing zeolite and their catalytic performance for combustion of hydrocarbons and NO conversion. The NO decomposition activity increased in order $n\text{-C}_{16} > n\text{-C}_{10} > n\text{-C}_8$ and this order was reversed of their combustibilities. To explain these results, a conceivable reaction mechanism, namely, microscopic sequential reaction mechanism, was proposed.

The combustion reaction, which is competing reaction with the NO decomposition reaction, combustion of hydrocarbon on metallosilicates were studied by Inui et al. [44]. They observed that the combustion activities were highly dependent on the elements introduced to the silicate crystals. High dispersion of the incorporated elements also contributed to the reaction. The metallosilicate catalysts showed higher performances than conventional catalysts, the advantages of metallosilicate, due to the high dispersion of the element, were suggested.

The redox properties of metallosilicates and their NO decomposition activities in oxidative or reductive atmosphere were investigated by Inui et al. [45]. They found that the activities of H-Fe-silicate and H-Ni-silicate which showed significant redox response were much influenced by the presence of oxygen, indicating the importance of the redox property of the catalysts for the reaction. A conceivable mechanism of this reaction was concluded as follows: hydrocarbons remove the surface oxygen to create a reduced active surface. NO is decomposed on this partially reduced surface into nitrogen and oxygen until the surface is converted with oxygen. The activity is maintained until all the active surface is diminished by the oxygen.

Inui et al. [46] studied the contribution of activity of metallosilicates. They found that the acid properties are concerned with the hydrocarbon combustion. According to the products distribution, the combustibility of the hydrocarbons in the reaction gas is verified. Thus the acid property contributes indirectly to the NO decomposition in the presence of oxygen and hydrocarbons.

Inui et al. [47] reported that cobalt-silicate is the highest activity among the tested. The NO decomposition in the presence of excess oxygen and a low concentration of hydrocarbons was examined on various metallosilicates under a condition of the space velocity as high as 30,000 h⁻¹.

Inui et al. [48] studied the effects of the presence of H₂O, CO₂, and SO₂ of Co-silicate for NO decomposition reaction. They found that the addition of H₂O suppressed the combustion of hydrocarbons; however none of H₂O, CO₂, or SO₂ hindered the NO decomposition reaction. Cobalt silicate was demonstrated to be one of practical catalysts for this reaction.

Inui et al. [49] found that the metallosilicates with BEA structure were successfully synthesized by hydrothermal method. This result suggests a possibility of various modifications of this analogy by this method. The synthesized bimetallosilicates with BEA structure demonstrated an advantage due to the combination of the elements. Thus bifunctional catalysts have a potential for NO removal from diesel and lean burn emission.

Iwamoto et al. [50] reported that ZSM-5 zeolites containing Cu²⁺ ions showed unusually high and steady state activity for the catalytic decomposition of nitric oxide; for degrees of conversions of nitric oxide, and of conversion into nitrogen and oxygen were 97, 85, and 70 % respectively, at 823 K with a contact time of 10.0 g s cm⁻³ over 73 % exchanged Cu-ZSM-5.

Iwamoto et al. [51] studied the catalytic activity of copper ion-exchanged Y type zeolites for the nitric oxide decomposition. They observed that catalytic activity of Y zeolite containing copper ions (CuY) for decomposition of nitric oxide was enhanced through additional exchange of other metal ions or evacuation treatment around 923-973 K. In the first case, Co^{3+} or Ni^{2+} ions increase the catalytic activity while Ca^{2+} , Mn^{2+} , Fe^{2+} , and Zn^{2+} diminish the catalytic activity of CuY. In the second case, the catalytic activity of CuY evacuated at 973 K was twice that of CuY without the evacuation treatment, which is discussed in connection with the increment of Cu ions active for the decomposition.

Iwamoto et al. [52] reported that repeated ion exchange of the ZSM-5 zeolite using aqueous copper(II) acetate solution was found to bring about excess loading of copper ions above 100% of exchange level. The catalytic activities of the resulting Cu-ZSM-5 zeolites for direct decomposition of nitric oxide were very high and increased with increasing exchange level. The activity did not decrease even after 30 h of continuous service.

Kagawa et al. [53] studied the direct decomposition of nitric oxide. They found that the coexistence of metal cations such as alkaline earth and transition metal cations with Cu ions in ZSM-5 zeolite promoted the catalytic activity of Cu ion for direct decomposition of nitric oxide at temperature above 450 °C. The promotion effect was found to depend on the ion exchange mode.

Iwamoto et al. [54] found that copper ion-exchanged ZSM-5 is the most active for the selective reduction of nitric oxide by ethene in the presence of oxygen at temperatures as low as 437-573 K among transition metal ion- and proton-exchanged zeolites, and Al_2O_3 . The order of active temperature regions of cation exchanged ZSM-5 was Cu (the most active temperature, 523 K) < Co (623 K) < H (673 K) < Ag (723-873 K) < Zn (873 K). The activity of copper ion-exchanged ZSM-5 zeolite did not decrease much even in a high

gas hourly space velocity (GHSV) regions more than 10,000 h⁻¹ while those of of proton-exchanged zeolites and Al₂O₃ greatly decreased in such high GHSV regions.

The removal of nitric oxide over copper ion-exchanged zeolite catalysts were studied by Iwamoto et al. [55]. They found that direct decomposition and selective reduction of nitric oxide over copper ion-exchanged zeolite catalysts are new methods for removal of nitric oxide. The copper ion exchanged zeolite (Cu-Z) was the most active catalyst for decomposition of nitric oxide. The activity of Cu-Z zeolites increased with increase in the exchange level. The zeolites with copper ion-exchange levels of 100% or more, which could be prepared by repeating ion exchange of the ZSM-5 zeolite using aqueous copper(II) acetate solution or addition of ammonia into the aqueous copper(II) nitrate solution, showed significantly high activity even in the presence of oxygen and high GHSV region. It was clarified concerning Cu-Z, by using IR, ESR, phosphorescence, TPD, and CO adsorption measurements that (1) the Cu²⁺ ions exchanged into zeolite were reduced to Cu⁺ and/or Cu⁺-Cu⁺ through evacuation at elevated temperature, (2) after exposure to oxygen at 773 K and subsequent evacuation, about 40% copper ions in zeolite existed as Cu⁺ ions. (3) the NO⁻ species formed by adsorption of NO on Cu⁺ would be and the intermediate in the NO decomposition, and (4) redox cycle of Cu⁺ ⇌ Cu²⁺ in the zeolite is probably a key step to achieve the decomposition reaction. Selective reduction of NO by hydrocarbon in the presence of oxygen was first found by them and Cu-Z was remarkably effective for NO removal at temperature as low as 523-673 K. The activity for this selective reduction in NO+C₃H₆+O₂ system was not poisoned very much by addition of SO₂. The conversion into nitrogen was changed to 85% (773K) in the presence of SO₂, from 100% in absence of SO₂ which is in contrast with the fact that the catalytic activity for direct decomposition NO was completely lost on adding the same amount of SO₂. Furthermore, the reduction rate over Cu-Z at 573 K was higher than those over H-zeolite and alumina catalysts at 723 and 773 K, respectively, which have been reported to be active, after findings by the authors.

Kagawa et al. [56] found that the coexistence of alkaline earth (Ca and Sr) and transition metal (Fe, Co and Ni) cations with Cu ions in ZSM-5 zeolite is effective in the promotion of the maximum activity and the expansion of the active temperature range for the reduction of nitric oxide with ethane in the presence of excess oxygen.

The mechanism of nitric oxide decomposition over Cu-ZSM-5 was reported by Shelef [57]. Cu-ZSM-5, a containing zeolite, catalytically decomposes nitric oxide at temperatures below those of other catalysts. A mechanism is proposed which is based on active sites consisting of coordinately unsaturated cupric (Cu^{2+}) ions in square planar configuration. These sites are posited to chemisorb nitric oxide molecules in the gem-dinitrosyl form. The pair of adsorbed NO molecules desorbs as nitrogen and oxygen. This mechanism accounts for the experimental behavior in chemisorption and decomposition with invoking a cyclical oxyreduction of surface sites.

Sasaki et al. [58] studied the role of coexisting oxygen in the selective reduction of nitric oxide by propane on H-zeolites, alumina, Cu-ZSM-5 zeolite and $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts. They found that in the case of H-zeolites and alumina, oxidation of NO to NO_2 played an important role for the overall selective reduction of NO. On the other hand, the initial reaction step was considered to be partial oxidation of propane over Cu-ZSM-5 and $\text{Pt}/\text{Al}_2\text{O}_3$.

Hall and Valyon [59] studied the mechanism of nitric oxide decomposition over Cu-ZSM-5. In the preceding Letter Shelef has proposed a mechanism for NO decomposition involving coordinately unsaturated Cu^{2+} sites on which NO molecules are chemisorbed in the gem-dinitrosyl form. At reaction temperature this complex is supposed to decompose into N_2 and O_2 without involving a redox process. That such a process is feasible has been pointed out by Moser. Shelef cited several reasons in support of this view and others that have led him to think that a cyclic redox mechanism is not operative. These arguments are

countered herein and some new data are presented showing the infrared spectra of surface species recorded under in situ reaction conditions.

d' Itri and Sachtler [60] studied the reduction of NO over impregnated Cu/ZSM-5 in the presence of O₂. They found that Cu/ZSM-5 catalysts prepared by impregnation of Cu acetate are active for NO reduction. In mixture containing both NO and O₂, reductants such as CO or CH₄ preferentially react with O₂, but propane react preferentially with NO. Small amounts of O₂ actually increase the reductant of NO by C₃H₈ oxidation the N₂ yield reaches a maximum near an O₂/C₃H₈ ratio = 5, i.e. the stoichiometry of total C₃H₈ oxidation. At much higher than stoichiometric O₂ content for total C₃H₈ oxidation N₂ yield with C₃H₈ (54%) is still substantially higher than, for instance, with CO of the same or larger concentration. The hypothesis that an intermediate of C₃H₈ oxidation is responsible for the enhanced NO reduction is then proposed. Temperature programmed reduction showed that after reaction with NO + C₃H₈ and sub-stoichiometric amounts of oxygen Cu in the catalyst is mainly metallic, but CuO particles appear to be formed in the presence of excess of O₂.

Burch and Millington [61] studied role of propane in the selective reduction of nitric oxide in copper exchanged zeolites. Gas switching experiments examining the first few minutes of reaction, have been used to study selective reduction of nitric oxide by propane on a Cu-ZSM-5 catalyst in an oxygen-rich mixture. They found that the conversion of nitric oxide to nitrogen reaches a steady-state activity in a very short period of time. It is concluded that carbon deposition is not responsible for conversion of nitric oxide into nitrogen. It is proposed in stead that the hydrocarbon oxygen act to maintain the active copper sites in an oxidation state suitable for direct nitric oxide decomposition.

Walker et al. [62] studied mechanism of the lean NO_x reaction over Cu/ZSM-5. Transient (including temporal analysis of products (TAP)) techniques have been used to probe the mechanism of the lean NO_x reaction over Cu/ZSM-5. The activation of propane

and nitric oxide by Cu/ZSM-5, in the presence and absence of oxygen, have been investigated by TAP to elucidate the nature of the reducing species involved in the formation of nitrogen. Propane is converted to long-lived (carbon-rich) species on the zeolite whether oxygen is present or not, and it is these deposited coke species which act as the reactant in these catalyst systems. The ability of the coke to reduce nitric oxide is significantly enhanced by the presence of oxygen. The crucial role of oxygen appears to be induce the generation of and adsorbed state of NO_x on the exchanged-Cu sites; these NO_2 -type species exist at temperatures characteristic of high lean NO_x activity. During temperature programmed reaction under a fuel lean (oxidizing) exhaust gas, both nitric oxide and propane are retained at lower temperatures; as the temperature rises, so propane retention(as coke) and total oxidation begin to complete. However, there are sufficient reducing species still present on the surface to allow substantial reduction of the NO_2 species, as the latter approach their limit of thermal stability.

The selective reduction of nitric oxide with hydrocarbons were studied by Hall et al. [63]. NO reduction with isobutane in the presence and absence of oxygen has been studied over Cu-ZSM-5-14-114 and compared to the simple decomposition reaction. In the presence of sufficient oxygen, complete combustion of hydrocarbon was observed, whereas in its absence, acid catalysis accompanied by dehydrogenation associated with coking occurred. The effect of adding nitric oxide to the HC/He stream in the absence of oxygen was small; the conversion to nitrogen was little affected by the hydrocarbon. When oxygen was added, however, the decomposition was complete at 573 K even at high space velocities(e.g., SVH ~10000) even though the combustion was not. Isobutane (an Alkane) was more effective than C_3H_6 (an alkene) for selective reduction; this is not generally the case. The presence of excess oxygen inhibited aging of the catalyst.

The oxidation state of Cu in Cu-ZSM-5 has been investigated by the X-ray absorption near edge-structure (XANES) spectroscopic method during NO decomposition

catalysis. Lui and Robota [64] studied and designed an in situ reactor system with which they can measure the relative NO decomposition rate while taking XANES spectra. They observed $1s \rightarrow 4p$ electronic transition of Cu(I) in Cu-ZSM-5 appears as a narrow, intense peak which is an effective measure of changes in the population of copper oxidation states. This transition is quite intense after Cu-ZSM-5 is activated in inert gas flow. However, its intensity decreases but by no means disappears after the admission of NO/N₂ gas mixture. They conducted the reaction in a temperature cycle around the optimum conversion temperature off 773 K and recorded the XANES at each temperature. They observed that the integrated intensity of Cu(I) $1s \rightarrow 4p$ transition, which is proportional to cuprous ion concentration in Cu-ZSM-5, was well correlated with the NO decomposition rate. This finding supports the conjecture that Cu(I) participates in a redox mechanism during catalyzed NO decomposition in Cu-ZSM-5 at elevated temperature.

Vayon and Hall [65] studied properties of Cu-ZSM-5 catalysts for nitric oxide decomposition. Equilibrium exchange isotherms were determined for the exchange of Cu²⁺ with NaZSM-5 at varying Cu acetate concentrations in solution of constant volume and zeolite weight. At low Cu²⁺ levels the solid scavenged or the copper ions. When copper could be detected in equilibrated solution, "over exchange" was observed. The extent of "over exchange" was higher at pH ~ 6 than at pH ~ 4. These results were analyzed in relation to catalytic activity.