CHAPTER II
LITERATURE REVIEW

Removal of NO in exhaust gases from diesel engines and other lean-burn combustion facilities has been one of the most important target for pollution control but up to now no practical methods have been developed. Thus, intensive effort has been made to over come this difficult. Recently, there had many reports about using of Cu/Na-ZSM5 and some other zeolite catalyst to catalyze the selective NO reduction. This chapter was summarized some of the researches in this area.

Hamada et al. [22] compared the catalytic activities of copper ion-exchanged ZSM-5 (Cu/ZSM-5) with other catalysts. They showed that the order of activity was Cu/ZSM-5 > Ag-Co$_3$O$_4$ > La-Sr-Co(Cu)-O > Pt/Al$_2$O$_3$ > Y-Ba-Cu-O/MgO. The extent of conversion over Cu/ZSM-5 was higher than those others at temperature as low as 500 °C. The results indicated that Cu/ZSM-5 was the most active catalyst at 500 °C for the decomposition of dilute NO gas.

Iwamoto et al. [23] found that the catalytic activity of one cupric ion exchanged into ZSM-5 zeolite was much higher than that in mordenite, ferrierite, and L-type zeolites. In addition, it was noted that the mordenite with molar ratio of SiO$_2$/Al$_2$O$_3$ = 18.9 showed higher catalytic activity than that with molar ratio of SiO$_2$/Al$_2$O$_3$ = 10.53, in spite of the smaller amount of copper ions included in the former than that in the latter. They suggested that the zeolite structure and the aluminum content (or SiO$_2$/Al$_2$O$_3$ molar ratio) were more important factors for controlling catalytic activity.

The selective reduction of nitric oxide by ethene in the presence of oxygen was studied by Iwamoto et al. [24]. They observed that copper ion-exchanged ZSM-5 zeolite was the most active at temperature as low as 200-300 °C compared with transition metal ion- and proton- exchanged zeolites, and Al$_2$O$_3$. The order of active temperature regions of cation-exchanged ZSM-5 zeolites was Cu (the most active temperature, 250°C) < Co (350°C) < H (400°C) < Ag (450-600°C) < Zn (600°C).

Moreover, the activity of copper ion-exchanged ZSM-5 zeolite did not decrease even in gas hourly space velocity (GHSV) of more than 10000 h^{-1}

Hamada et al. [10] studied the selective reduction of nitric oxide with hydrocarbons over zeolites catalysts in an oxygen rich atmosphere. The most active catalyst of the three H-form zeolites was H-mordenite, which gave the maximum nitric oxide conversion of 65% at 350 °C, followed by H-ZSM-5 and HY. It was interesting that Na-ZSM-5 and silicalite were also active for the reaction although the activity was not so high. On the other hand, silica gel showed no activity. For each catalyst, the percentage conversion of nitric oxide to nitrogen had a maximum value at a certain reaction temperature. This optimum temperature varied with the type of zeolite catalysts. The use of propene instead of propane as the reducing agent lowered this temperature for H-ZSM-5 and HY. This suggested that the efficiency of the selective reduction depended not only on the reduction temperature but also on the type of zeolites and hydrocarbons.

The removal of nitric oxide over copper ion-exchanged zeolite catalysts were studied by Iwamoto et al. [25]. They found that 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 zeolite 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. Characterization of Cu/Z, by using infrared spectroscopy (IR), electron spin resonance (ESR), phosphores, temperature programmed desorption measurements indicated that (1) the Cu^{2+} ions exchanged into zeolite were reduced to Cu^+ and/or Cu^+-Cu^+ through evacuation at elevated temperature, (2) after exposure to oxygen at 500 °C 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 an intermediate in the NO decomposition, and (4) redox cycle of Cu^+=Cu^{2+} in the zeolite was 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 affective for NO removal at temperature as low as 250-400 °C. Furthermore, they had reported that the NO reduction rate over Cu/Z at 300 °C was higher than those over H-zeolite and alumina catalysts at 450 and 500 °C, respectively.

Iwamoto and Mizuno [26] studied catalytic activity of copper ion exchanged ZSM-5 (Cu/ZSM-5) for NO reduction. They found that the activity of Cu/ZSM-5 depended on the exchange level of copper ion. The activity increased with the increment of the exchange level, reached a maximum at the exchange level of 80-100% and then decreased a little.

Hamada et al. [27] investigated mechanism of the selective reduction of nitric oxide with propane by Cu/ZSM-5. They suggested that nitric oxide was oxidized to nitrogen dioxide intermediate which was subsequently reduced to nitrogen by reaction with propane. The direct oxidation of propane with oxygen was a side reaction. Probably the high selectivity of the reduction was cause by the higher activity of nitrogen dioxide to hydrocarbons than that of oxygen. Moreover, they suggested that the decrease in nitric oxide conversion to nitrogen at high temperatures could be explained by the higher rate of propane-oxygen reaction.

The catalytic activity of Cu/ZSM-5 (Cu exchanged extent from 23 to 210%) and Cu/Y (Cu exchanged extent from 5 to 100%) zeolites in NO decomposition at 500 °C was studied by Campa et al. [28]. The results showed that the decomposition rate increased by roughly 100 fold when the extent of exchange with copper in the ZSM-5 framework increased form 20% to 100%. This phenomena showed that not all Cu sites were equivalent in their decomposition activity. In addition, they found that Cu-Na-ZSM-5, which was prepared by impregnation, was as active for NO decomposition as ion-exchanged ZSM-5 catalysts when the excess copper in Cu-Na-ZSM-5 was removed by H_2O washing after impregnation.

The catalytic reduction of NO_x in actual diesel engine exhaust over copper ion-exchanged ZSM-5 zeolite catalyst in the presence of oxygen and hydrocarbons were reported by Iwamoto et al. [29]. Copper ion exchanged ZSM-5 zeolite effectively reduced NO_x by 25% in normal engine operation, and by 40% when C_2H_4, C_3H_6, or

C_4H_8 was added. The temperature of maximum activation was observed at 400 ° C irrespective of hydrocarbon species. However, the effect of CH_4 was small, indicating that the reduction effect depended on the type of hydrocarbon.

G.P. Ansell et al. [30] studied mechanism of the lean NO reaction over Cu/ZSM-5 by used transient techniques (included TAP, Temporal Analysis of Products). The activation of propene 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. Propene was converted to long-lived (carbon-rich) species on the zeolite whether oxygen was present or not, and it was these deposited species which acted as a reductant in this catalyst system. The ability of coke to reduce nitric oxide was significantly enhanced by the presence of oxygen. The crucial role of the oxygen appeared to be to induce the generation of an adsorbstate of NO_x on the exchanged-Cu sites; these NO_2-type species existed at temperatures characteristic of high lean NO_x activity. During temperature-programmed reaction under a fuel-lean (oxidizing) exhaust gas, both nitric oxide and propene were retained at lower temperature; as the temperature rose, so propene retention (as coke) and total oxidation begin to complete. However, there were 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.

I. Halasz, A. Brenner, and K.Y. Simon Ng [31] studied about active site of H-ZSM5 catalysts for the oxidation of nitric oxide by oxygen. They compared the catalytic activities of H-ZSM5-18, H-ZSM5-150, Li-ZSM5-18, and H-Mag (numerical suffixes mark the Si/Al ratios of zeolites, H-Mag is the proton exchanged form of the layered sodium silicate, magadiite) for the oxidation of NO by O_2 at different ratios of reactants at temperatures from 25 to 600 °C. H-ZSM5-18 typically had activity maxima near 25 and 400 °C at most O_2/NO reactant ratios. Regardless of the partial pressures of reactants, NO + 1/2 O_2 $\leftrightarrow$ NO_2 equilibria were attained at 400 °C and above. The H-ZSM5-150 and Li-ZSM5-18 zeolites were only active at temperature near 25 °C, H-mag was practically inactive at the reaction conditions used. Their result indicated that Lewis acidic lattice aluminium ions and silanol hydroxyls were not

active in the oxidation of NO to NO_2 over H-ZSM5 zeolites. Brønsted acidic bridging hydroxyls were probably active sites for this reaction at temperature above 200 °C.

M. Sasaki et al. [32] studied role of oxygen in selective reduction of nitrogen monoxide by propane over zeolite and alumina-based catalysts (H-zeolites, alumina, Cu-ZSM5 zeolite and Pt/Al_2O_3). 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 initial reaction step was considered to be partial oxidation of propane over Cu-ZSM5 and Pt/Al_2O_3.

C.J. Bennett et al. [18] used temperature-programmed reaction traces for Cu/ZSM-5 heated under an oxidizing exhaust-gas were not consistent with the hydrocarbon acting as a direct reductant of NO. The results were reconciled by a surface mechanism in which hydrocarbon generated a reactive intermediate capable of reducing NO, but which itself could depleted by oxidation. This intermediate may be partial oxidation product of the hydrocarbon, or deposited coke, it did not appear to be CO.

J.L. Ditri and W.M.H. Sachtler [33] studied the role of oxygen in selective reduction of nitrogen monoxide by either propane or propene over "excessively" ion-exchange Cu/ZSM-5 has been studied. In a wide temperature region and in the absence of additives such as steam, propane was a more effective reductant than propene; with propane in the presence of oxygen reduction of nitric oxide to nitrogen approaches 100% above 327 °C. The difference in effectiveness was due to the difference degree of catalyst deactivation by carbonaceous deposits: more carbonaceous material is deposited from propene than from propane. Temperature-programmed oxidation shows that above 327 °C the rate of oxidation of carbonaceous deposits by oxygen is significant. The amount of such carbonaceous deposits was, therefore, lower when catalytic tests above 327 °C were done in the presence of oxygen. At very high temperatures, the in-situ volatilization of the deposits by reaction with oxygen kept the catalyst surface clean in the steady state of nitric oxide reduction.

V.A. Bell et al. [34] used high temperature in-situ FTIR to investigate the surface species present on Cu/ZSM-5 during the reduction of NO with propylene in

lean environment. Parallels have been observed between adsorbed surface species and catalytic activity for this reaction. Species detected at low temperatures were not representative of those detected at high temperatures where the catalyst was active. An oxidized nitrogen-containing species has been observed at 2580 cm^{-1} on Cu during reactions conditions (400 °C). In contrast, at low temperatures, where the catalyst was less active, coke and Cu^{+}-CO predominated. The effects of Cu weight loading, C/NO ratio, reaction temperature, and catalyst deactivation by steaming have been investigated with IR.

M. Guyon et al. [35] used two-step experiments to investigate the mechanism of NO reduction over copper ion-exchanged ZSM-5 zeolites. The first step was the formation of reactive intermediate and the second one the reaction of the intermediate during a transient regime without any hydrocarbon injection. the presence of NO or NO$_2$ appears to be mandatory to obtain such an intermediate. In contrast, the presence of oxygen is not necessary. The intermediate reacted only with NO$_2$ as well as with O$_2$. The role of oxygen could be to oxidize NO to NO$_2$ in a first reaction step.

F. Radtke et al. [36] found that hydrogen cyanide was formed over Cu/ZSM-5 during the selective catalytic reduction of NO$_x$ by either propene or ethene in the temperature range 177-327 °C. Under the reaction conditions used (reactant feed: 973 ppm NO, 907 ppm propene or 1448 ppm ethene, 2 % oxygen, W/F = 0.1 g s cm^{-3}), the concentration of hydrogen cyanide reach 20 and 30 ppm, respectively, depending on whether ethene or propene are used as hydrocarbons. In addition, significant N$_2$O formation was observed at temperatures lower than 427 °C, independent of the hydrocarbon used.

N.W.Hayes et al. [37] studied the adsorption and subsequent reaction of nitric oxide, propene, molecular oxygen and combinations of these gases has been studied on samples of Cu-ZSM5 catalysts of high activity in the selective reduction of NO by hydrocarbons, using infrared spectroscopy. When only propene was adsorbed, it first formed an adsorbed allyl and then undergoes stepwise oxidation to adsorbed acrolein, carboxylic acid species and carbon oxides. Since no gas phase oxygen was present, these oxidations involved extra lattice oxygen from the zeolite. These steps

highlighted the importance of small, oxygen containing copper clusters in the reaction. Exposure of fresh catalyst to NO and propene resulted in the formation of an organic nitro compound, as well as the species observed for propene alone . No coordinated NO or dimeric species, which they had been reported in their works previously. Almost identical results are observed for the full gas mixture of propene, NO and oxygen, in helium. To probe the possible role of nitro species in the reaction pathway, the interaction of nitromethane with the catalyst has been studied on nitromethane decomposed selectively, liberating nitrogen in the presence of oxygen over both Cu-ZSM5 and H-ZSM5 catalysts. They proposed that organic nitro compounds are important intermediates in the reaction, and speculate on a decomposition path way of nitrogen, based on known organic chemistry, which passed through dinitroso species. Nitriles were proposed to form under reducing conditions, but these may also decompose on exposure to oxygen, liberating nitrogen.

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D.H. Kim et al. [38] used FTIR to measure activities and identified the intermediate formed during the SCR of NO by propene over Cu/ZSM5. The band at 1624 cm^{-1} assigned to NO_2 species adsorbed on Cu(II) was observed after exposing Cu-ZSM5 to NO or NO and O_2 at 350 °C. The band at 2250 cm^{-1} assigned to -CN and/or -NCO species was observed during the SCR at 350 °C. The NO_2 species adsorbed on Cu ions was reduced to produce N_2 by the reaction with propene. When -NCO was exposed to NO and O_2 at 400 °C, the rate formation of the band at 1624 cm^{-1} was much faster than that of decrease of the band at 2250 cm^{-1}, indicating that the site for NO_2 formation was different from the site occupied by -NCO. The -NCO

identified by the band at 2250 cm^{-1} was involved in the slow catalytic cycle, while the NO$_2$ species was involved in the fast catalytic cycle.

The reviewed papers demonstrate that copper ion-exchanged ZSM5 zeolite (Cu/ZSM5) has capacity to selectively reduce nitric oxide with hydrocarbon in the presence of excess oxygen [18, 22-30, 32-38] although the mechanism of this reaction was not cleared. There were many researchers proposed the mechanisms which can be classified as follows:
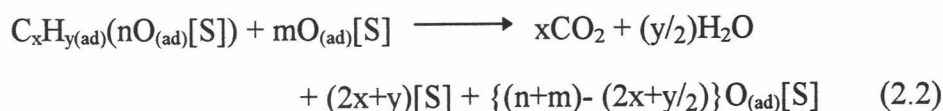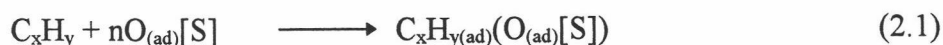
a) Nitrogen monoxide decomposition to yield nitrogen and oxygen (with the hydrocarbon acting to regenerate the active sites by removing surface oxygen) [45].

b) Deposition of carbonaceous material [18,30] which becomes the catalytically active surface.

c) Preferential reaction between nitrogen dioxide formed from nitrogen monoxide and oxygen and the hydrocarbon reducing agent [27,48].

d) Partial oxidation of the hydrocarbon to form reaction intermediates capable of the selective reduction of nitrogen monoxide [18,48-50].

From these four mechanisms, (a) is often rejected since oxygen is found to promote the selective catalytic reduction of nitrogen oxide by hydrocarbons. However, it is only valid to reject this mechanism if the original hydrocarbon was simply responsible for removing the surface oxygen. It does not preclude a process in which a partially oxidized hydrocarbon intermediate species responsible for performing this role. Equally, it does not preclude a mechanism in which some oxygen is required to prevent the complete reduction of an active ionic species(e.g., Cu$^+$) to the metal. Thus, Inui et al.[46], based on studies of nitrogen monoxide decomposition in the presence of excess oxygen and cetane, have proposed a related mechanism in which the hydrocarbon reduce surface oxygen to produce vacant active sites [S]:

$$C_xH_y + nO_{(ad)}[S] \longrightarrow C_xH_{y(ad)}(O_{(ad)}[S]) \qquad (2.1)$$

$$C_xH_{y(ad)}(nO_{(ad)}[S]) + mO_{(ad)}[S] \longrightarrow xCO_2 + (y/2)H_2O$$
$$+ (2x+y)[S] + \{(n+m)-(2x+y/2)\}O_{(ad)}[S] \qquad (2.2)$$

Byong K. Cho [47] encouraged this mechanism by their experiment which NO decomposition activity of Cu/ZSM-5 has been shown to be sufficiently high on reduced Cu/ZSM-5. Their observation could be summarized in the following simplified reaction mechanism for reaction with ethylene:

- NO decomposition on Cu surface:

$$NO + S \longrightarrow NO_a \qquad (2.3)$$

$$2NO_a + 2S \longrightarrow 1/2\ N_2 + 2\ O_a \qquad (2.4)$$

$$O_a + O_a \longrightarrow O_2 + 2S \qquad (2.5)$$

- Ethylene adsorption on ZSM-5:

$$C_2H_4 + S' \longrightarrow C_2H_{4a} \qquad (2.6)$$

- Ethylene oxidation on interface:

$$C_2H_{4a} + 6O_a \longrightarrow 2CO_2 + 2\ H_2O + 6S + S' \qquad (2.7)$$
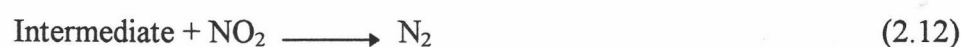
In the chemical equations S and S' denoted the NO adsorption site on Cu and C_2H_4 adsorption site on ZSM-5, respectively. the mark "a" denoted that chemicals are adsorption reactants.

With regard to the reaction scheme (b) above, there are both agreement and disagreement. The disagreement are from experiments showing carbon balance of greater than 98 % [20] have led some workers to conclude that no carbon deposition is occurring under the condition of reaction. Many works use transient technique to determined the mechanism of this reaction and agree with carbon deposited are the reaction intermediate. The examples are such as G.P. Ansell et al. [30], M. Guyon et al.[35], and etc. The experiments of G.P. Ansell et al. [30] performed on TAP, temporal analysis of products, to probe the mechanism of this reaction. The TAP technique use pulse reactant to microreactor and detect the product by a quadrupole mass spectrometer detector in function of time on stream. They concluded that the key intermediates in SCR on Cu/ZSM-5 were coke (formed on the zeolite component) and NO_2-type species (formed on the exchanged copper sites) and the role of oxygen is
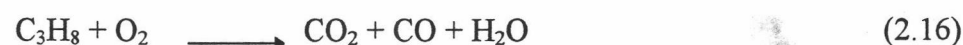
not relevant to the activation of the hydrocarbon, but it is crucial to the formation of the Cu-NO$_2$ species. Recently, M. Guyon et al. [35] used the two step experiment to investigate the mechanism of SCR on Cu/ZSM-5. The first step, devoted to the intermediate formation, was performed under different gas mixtures. The second step, hydrocarbon were no longer injected, in order to investigate whether the intermediate possibly formed during the first step was able to reduce NO or NO$_2$. Their main conclusions could be summarized as follows

- A reactive intermediate is only generated over the catalyst from NO or NO$_2$ and propene. The injection of O$_2$ is not mandatory.
- This intermediate only reacts with NO$_2$, not with NO, to give nitrogen.
- Oxygen allows the oxidation of NO to NO$_2$ and competes with NO$_2$ to react with the intermediate.

An overall mechanism for SCR over Cu/ZSM-5 propose by them.

$$NO + O_2 \longrightarrow NO_2 \tag{2.8}$$

$$NO_2 \longrightarrow NO + O_2 \tag{2.9}$$

$$NO + HC \longrightarrow Intermediate \tag{2.10}$$

$$NO_2 + HC \longrightarrow Intermediate \tag{2.11}$$

$$Intermediate + NO_2 \longrightarrow N_2 \tag{2.12}$$

$$Intermediate + O_2 \longrightarrow Oxidation\ products\ (CO, CO_2, ...) \tag{2.13}$$

Reaction scheme (c), in case of the experiment by Hamada[27, 48], it was clearly that the reduction by propane of nitrogen dioxide to nitrogen was easier than that nitric oxide over H-ZSM-5 as well as alumina. They suggested the reaction scheme as follow:

$$NO + O_2 \longrightarrow NO_2 \tag{2.14}$$

$$NO_2 + C_3H_8 \longrightarrow N_2 + CO_2 + CO + H_2O \tag{2.15}$$

$$C_3H_8 + O_2 \longrightarrow CO_2 + CO + H_2O \tag{2.16}$$

M. Sasaki et al. [31] performed the experiment with various reactants and catalysts. They concluded that oxidation of NO to NO_2 played the important role for SCR on H-ZSM-5. Further more, M. Guyon et al. [35] showed the clearly results that NO_2 reacted with intermediate from first step (see experimental description from scheme (b) above) better than NO. Furthermore, D.H. Kim et al. [38] used in-situ FTIR for identified the reaction intermediates of SCR. They concluded that the SCR proceed through the reduction of NO_2 adsorbed on Cu(II) ions by propene as main reaction. However, they found that the -NCO species as a kind of nitro-organic complex identified by IR band at 2250 cm^{-1} reacted slowly with NO and O_2 to produce N_2 and CO_2, suggested that -NCO species was involved in the slow catalytic cycle. Its reactivity with NO and O_2 was too low for -NCO to be main reaction intermediate.

A number of papers have favored the suggestion in scheme (d) that partially oxidized intermediates formed from the hydrocarbon reductant are effective in the selective reduction of nitrogen monoxide. [18,48-50]

This study investigate the effect of coke to the reaction activity of ZSM-5 catalyst (or MFI catalyst). Based on the idea that coke formation on the active site may cause the decreasing of activity of the catalyst, the experiment perform by use propylene to form coke on the catalyst surface. Then, both fresh and spent catalysts was characterized by various methods, such as TPO(Temperature Programmed Oxidation), acid sites measurement by pyridine adsorption, etc.. The study of coke may explain the mechanism of selective reduction of NO with propylene on zeolite catalyst.