

CHAPTER II

LITERATURE REVIEWS

Selective catalytic reduction(SCR) of nitric oxide(NO) by hydrocarbon in an oxidizing atmosphere has been promised as a process for NO removal in the exhaust gas of lean-burning engines. Although Brown [38] mentioned that nitric oxide reacted readily with liquid isobutylene to give nitrogen and a mixture of nitrated products in 1956, the works of Iwamoto et al. [10] and Held et al.[6] on the reduction of NO by hydrocarbon gas brought this topic into world wide study just in 1990.

In the work of Iwamoto et al.[11,13], copper ion-exchanged ZSM-5 (Cu/ZSM-5 or Cu/MFI) was not only found to be active for the decomposition of NO but it active also for reduction of NO by hydrocarbon. Iwamoto et al.[12,14,17] compared the activity of various metal ion-exchanged ZSM-5 on the SCR of NO. The order of the maximum activity was $Cu \approx Co \approx H \approx Ag \approx Zn > Mn \approx Ni \approx La \approx Ca \approx Pd > Cr$. Among the most active metal/ZSM-5 zeolites, the order of minimum active temperature regions was $Cu(250\text{ }^{\circ}C) < Co(350\text{ }^{\circ}C) < H(400\text{ }^{\circ}C) < Ag(450 - 600\text{ }^{\circ}C)$. The activities of copper exchanged with various types of zeolites were also investigated. The order of activities at 250 °C in the NO(1000 ppm) + C₂H₄(250 ppm) + O₂(2 %) system was as follows: Cu/ZSM-5 > Cu/MOR > Cu/LTL > Cu/FER > Cu/Y. Furthermore, in comparing types of catalysts[39], it was found that Cu/ZSM-5 was more active than Cu/Al₂O₃. These results indicated the outstanding activity of Cu/ZSM-5 compared with the other catalysts in the selective reduction of NO by hydrocarbons. Moreover, Zhang et al.[41] studied the reversible and irreversible adsorption of nitrogen monoxide on copper ion exchanged zeolites. They noticed that the order of the NO adsorption capacity on zeolites was as follows: Cu/ZSM-5 > Cu/MOR > Cu/FER > Cu/LTL > Cu/Y which ,interestingly, is similar to the order of activity in the SCR of NO suggested by Iwamoto et al.[14,17]. From above

observations, Cu/ZSM-5 is likely to be one of the most active catalysts for the selective reduction of NO by hydrocarbon.

In the system of NO, C₃H₆ and O₂ over Cu/ZSM-5[11-13], the conversion of NO typically began to occur at 227 °C and reached a maximum at about 277 °C and then decreased at higher temperature while hydrocarbon conversion became 100 % at around 427 °C.

It was found additionally that the concentration of O₂[11,13,15], level of copper exchange[12, 14, 17], space velocity[14, 15, 17] all significantly effected the catalyst activity in the NO reduction. The conversion of NO in the reduction of NO in the presence of O₂ was much higher than in the absence of O₂[11,13,15]. The conversion level of NO drastically increased with the increase of O₂ concentration. The activity of Cu/ZSM-5 also depended on the exchange level of copper ion. The activity rose with the increment of the exchange level and reached a maximum at the exchange level of 80 -100 % and then slightly decreased. The degree of ion exchange level was calculated by the equation[15] as shown below:

$$\% \text{ ion exchange} = \frac{(\text{oxidation number of cation}) \times (\text{number of cations})}{(\text{number of Al ion in zeolite})} \quad (2.1)$$

In the consideration of the space velocity, the activity of Cu/ZSM-5 was slightly enhanced at higher space velocity whereas the activities of Cu/Al₂O₃ and H/ZSM-5 dropped rapidly [14,15,17].

H/ZSM-5 was firstly proposed by Hamada et al.[22] as an active catalyst for the SCR of NO. Since this non-metal catalyst is cheaper than other metal catalysts, H-ZSM-5 has been quite widely studied so far[22-24, 42, 43]. In contrast, Na-ZSM-5 was not active at all in the NO reduction[16, 22, 35]. Hamada et al.[23] suggested that the acid site on H-ZSM-5 might play the major role as the active site for the SCR.

There have been several mechanisms suggested for the SCR of NO by hydrocarbons. They can be classified by their main features.

Iwamoto et al.[14] found that the $\text{NO} + \text{C}_2\text{H}_4 + \text{O}_2$ and $\text{NO}_2 + \text{C}_2\text{H}_4 + \text{O}_2$ systems, different trend of NO conversion appeared whereas hydrocarbon conversion in the $\text{C}_2\text{H}_4 + \text{O}_2$ and $\text{NO} + \text{C}_2\text{H}_4 + \text{O}_2$ system were almost the same. Therefore, they suggested that the first step of the SCR reaction would be the partial oxidation of hydrocarbon with O_2 to form an oxygenated hydrocarbon which served as the intermediate in the reaction. NO would preferably interact with this intermediate rather than hydrocarbon to produce dinitrogen and CO_2 which are the final products of the NO removal process. Montreuil and Shelef[16] observed that a partial oxidation specie could reduce NO in the absence of oxygen atmosphere. This strongly supported the important role of oxygenated hydrocarbon in the reduction of NO by hydrocarbon in an excess oxygen condition. In addition, the study of Bennett et al.[44] which concerned the steady state kinetics of NO reduction over Cu/ZSM-5, indicated that the intermediate of the reduction might be a partial oxidation product of hydrocarbon. Kharas's study[45] agreed with this mechanism as well.

Hamada et al.[46] suggested that NO_2 was an intermediate of the SCR of NO over H-ZSM-5 and alumina based catalysts. Shelef et al.[47] also suggested that the oxidation of NO to NO_2 might be the first step of the SCR. NO_2 was then reduced by hydrocarbon to form N_2 and CO_2 . Using Cu/ZSM-5 Petunchi and Hall[48] compared the reactions between hydrocarbons and NO and NO_2 . They mentioned the critical role of NO_2 in the reaction mechanism. A FT-IR study of Beutel et al.[49] suggested that NO_y ($y \geq 2$) was able to abstract H atoms from hydrocarbon molecules. Charjar et al.[50] noticed that the reduction of NO_2 by propane could occur in absence of oxygen. Furthermore, The works of Yokoyama and Misono[35] and Guyon et al.[51] supported NO_2 formation as a the first step in selective reduction of NO.

Ansell et al.[52] proposed that carbonaceous deposits were a key intermediate of the lean NO_x reaction over Cu/ZSM-5. From their temporal-analysis-of-products (TAP) experiments, they suggested that the reduction is the interaction between coke which formed on the zeolite component and an NO_2 type species which formed on the

exchanged copper sites. Shelef [3] proposed that the Cu/ZSM-5 catalyst is bifunctional. He noticed that Brønsted acid sites on ZSM-5 activated hydrocarbons via oligomerization while copper sites activated NO to form NO_2 .

However, the gas switching experiments of Burch and Millington[53] showed that the conversion of NO to N_2 reached steady state in a very short period of time. Therefore, the carbon deposition might not be responsible for the NO reduction to N_2 . They proposed instead that the reaction was a redox process in which decomposition of NO occurs and hydrocarbon removes adsorbed oxygen to maintain the active site in a suitable state [53, 54]. Cho [55] also supported this mechanism. He suggested that the reaction mechanism of NO reduction involved the NO decomposition which accompanied with hydrocarbon oxidation[55]. The decomposition of NO was accomplished at Cu sites whereas hydrocarbon adsorbed on ZSM-5. The critical role of hydrocarbon adsorbed on ZSM-5 was to scavenge oxygen from the active sites in the high temperature regime, regenerating these sites for NO decomposition.

Many other intermediates in the reduction of NO by hydrocarbon have been proposed. Table 2.1 shows some of the proposed intermediates in the Cu/ZSM-5 catalysis of the SCR of NO by hydrocarbons.

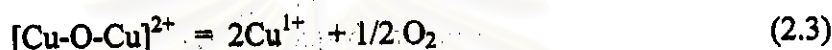
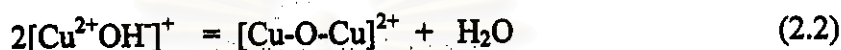
The characteristics of valence the catalytic surface of the deNO_x catalysts have been widely studied. The copper ion on ZSM-5 was investigated. Normally, oxidation states of copper are either +1 (Cuprous ion) or +2 (Cupric ion). Sass and Kevan[68] studied the copper ion exchanged ZSM-5 using electron spin echo modulation (ESEM). They observed that, at low Si/Al ratios, one Cu^{2+} ion exchanged for two monovalent cations and was located approximately halfway between two Al atoms, while at high Si/Al ratios, Cu^{2+} located nearer to one Al atom.

Table 2.1 Proposed intermediates in the reduction of NO by hydrocarbon over Cu/ZSM-5.

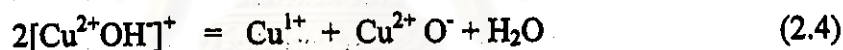
Intermediates	References
CN	[56]
NCO	[57,58]
HNCO	[59]
ChxNyOz	[60]
organic nitro, nitrite compounds , nitroso compounds	[61]
acrolein, azoxy, organo-nitro compounds	[62]
$\text{Cu}^{2+}\text{-NO}, \text{NO}^{3-}$	[63]
$\text{Cu-O-NO}_2, \text{NO}_{2,\text{phys}}$	[48]
$\text{C}_x\text{H}_y\text{O}_z, \text{NO}_x$	[64]
carboxylate, N_xO_y	[65]
NH_3	[66,67]

Photoluminescence study of Dedecek and Wichterlova [69] concurred with Sass and Kevan's study. Furthermore, Dedecek and Wichterlova investigated the reducibility of copper ions in Cu/H-ZSM-5. They suggested that Cu^{2+} could be reduced in hydrogen to form Cu^{1+} and Cu^0 whereas, in CO atmosphere, Cu^{2+} could be reduced practically only to Cu^+ . Moreover, it was also found that Cu^{2+} could be reduced to Cu^+ by a thermal vacuum treatment [70-73] but more easily in the presence of water [74], in an inert flow at high temperature [73] and even in an NO gas system [70,74]. However, Cu^{1+} or Cu^0 can be reoxidized to Cu^{2+} in a suitable oxidizing condition as well.

In studies of surface species on Cu/ZSM-5, Valyon and Hall[75,76] mentioned the existence of extralattice oxygen (ELO) which is carried into the catalysts during preparation as water of cation hydration or in some form as $[\text{Cu}^{2+}\text{OH}^1]^+$ and H^+ . This CuOH^+ is eliminated by dehydroxylation at high temperature to produce $[\text{Cu-O-Cu}]^{2+}$ specie and Larsen et al.[71] mentioned that this species could be reduced to Cu^{1+} as below:



Moreover, they [71] proposed a mechanism for autoreduction to Cu^{2+} and Cu^{1+} as follow:



Ciambelli et al.[74] suggested that Cu^{2+} was reduced in vacuum and H_2O played the significant role in this reduction of copper. They also studied the activities of Cu/ZSM-5 at various level of copper exchange and found some copper on the surface of Cu over exchanged ZSM-5 ($> 200\%$), which has the highest activity, formed CuO , while some formed a complex ion as polymetric species at an Al tetrahedral and some exchanged at a defect site such as a nested silanol group. That was the reason that the over exchanging is possible.

Grunert et al.[37] identified six different copper species existing in Cu/ZSM-5, differing in their environment, degree of aggregation, or location from their study using electron spectroscopy and X-ray adsorption spectroscopy. Observation of binding and Auger kinetic energies[37] also illustrated that copper becomes dispersed in the zeolite channels, in the form of both isolated, 5-fold coordinate ions and small clusters containing extralattice oxygen.

Not only copper species but also residual cations are on the Cu/ZSM-5 surface. Protons on ZSM-5 are always in form of hydroxyl groups bonded to aluminum tetrahedrals as so-called Brønsted acidic bridging hydroxyl groups (BA-OH) [77]. Halasz et al. [43] suggested that, in H-ZSM-5, only 50 % of aluminum tetrahedral acts as Brønsted acid site. 25 % of all aluminum is extralattice and will dominate another 25 % of the remaining Al. Janchen et al. [78] studied H MAS NMR of metal exchanged zeolites and suggested that the chemical composition of the lattice significantly effect on the acidic strength of the Brønsted sites whereas differences in structure or pore size play a much small role. Since two Brønsted sites can be dehydroxylated to produce one Lewis acid site, there generally are both Brønsted and Lewis acidic sites on the catalysts surface.

The interaction between nitric oxide and a copper site on ZSM-5 has been widely studied. From the EPR and IR investigation of Giamello et al. [79], it was found that NO reacted typically with $\text{Cu}^{2+}/\text{ZSM-5}$ by partial electron transfer from the molecule to the transition metal while the interaction of NO with $\text{Cu}^+/\text{ZSM-5}$ was characterized by the initial formation of a mononitrosyl without electron transfer to the copper. This specie also led to the formation of a dinitrosyl group. Spoto et al. [80,81] worked on $\text{Cu}^+/\text{ZSM-5}$ prepared by ion-exchanging H-ZSM-5 with gaseous CuCl. They noticed that Cu^+ ions were poorly coordinately and could form $\text{Cu}(\text{CO})_n$, $n = 1, 2, 3$ carboxylic and $\text{Cu}^+(\text{NO})_n$, $n = 1$ or 2 nitrosyl complexes. $\text{Cu}^+(\text{NO})_2$ were unstable at room temperature and would form nitrous, NO_2^- and oxidized Cu^{2+} -NO species. Moreover, Wichterlova et al. [82] found that Cu ions in vicinity of the Al framework were able to form stable Cu^+ -dinitrosyl complexes where abundant in the ZSM-5 structure. They are responsible for the high activity in NO decomposition, whereas Cu ions neighboring two Al atoms in the framework formed mostly mononitrosyl complexes, which provided a high activity in the selective reduction of NO. Nevertheless, Cheung et al. [83] mentioned that the catalytic activity of Cu-zeolite appeared to depend on the Cu^{1+} - Cu^{2+} redox cycle which result in an ON-Cu^{2+} - NO^{2-} complex postulated as the intermediate of the decomposition of NO.

In addition, in situ FT-IR in the reactions of NO and O₂ on various types of ZSM-5 catalysts was used by Szanyi and Paffett [84]. They found that NO₂ could adsorb on Brønsted acidic sites but NO could adsorb both on Cu⁺ and Cu²⁺ and further form NO₂ species. CO adsorb only on CuO, Cu metal and Cu¹⁺, however, CuO and Cu metal were not observed in their study[84]. Furthermore, they found that NO oxidation by oxygen could occur on H-ZSM-5 and NaH-ZSM-5 to form NO₂, N₂O₄ and N₂O₃ while, on Cu-ZSM-5, NO₂ was produced in both NO and NO + O₂ systems. This also agreed with the study of Kim et al. [58].

During the lean NO reaction, adsorbed species were investigated by Hayes et al.[56]. They observed the formation of aliphatic-cyanides species during the SCR of NO by hydrocarbon over Cu/ZSM-5. Kucherov et al.[85] showed that under typical conditions of selective catalytic reduction with a large excess of oxygen, all of copper is present in the Cu²⁺ state. This thus supported as a significant active site a square-plane isolated cupric ions. In the absence of oxygen, they found that Cu²⁺ ion was quickly reduced and possibly formed Cu⁰ crystallites leading to deactivation of the catalyst. These accord with a study of Petunchi and Hall[86]. However, the latter [86] also noticed that in the absence of oxygen, Cu²⁺ was reduce to Cu¹⁺ and partly to Cu⁰, a coke deposit was formed and the NO conversion was very low. While, with excess oxygen in the feed, Cu could be reoxidized to Cu²⁺, coke was cleaned up and the activity of catalyst was returned to correspond with 100 % NO conversion.

The tolerance of Cu/ZSM-5 in the presence of water and sulfur dioxide was studied by several researchers. Iwamoto et al. [15] found that, in the NO reduction by propylene over Cu/ZSM-5, the NO conversion to N₂ decreased as soon as steam was added in the reactant feed, but its activity would return when water vapor was removed from the feed. However, very high temperature treatment (600 - 800 °C) brought about substantial loss of micropore volume[87]. Kharas et al. [87] suggested that CuO crystallites growth primarily in destruction may be the main cause of the loss of micropore volume[87]. Volume loss appeared to be the primary cause of deactivation of Cu/ZSM-5[87]. Tabata et al.[87] noticed that neither dealumination, carbon deposition nor loss of micropore was observed in Cu-ZSM-5 samples after

they were treated under conditions simulating an exhaust stream. They therefore suggested that CuO cluster formation leads to deterioration of the activity of Cu/ZSM-5. Martinez et al.[89] found a reversible deactivation of Cu/ZSM-5 under wet conditions. Irreversible deactivation of the catalyst was also observed after testing more than 15 hr. on stream. However, Crambelli et al.[74] characterized fresh Cu/ZSM-5 catalysts and found that at the 556 % copper exchange level the catalyst contained divalent copper, but did not find any evidence for the presence of segregate CuO phases. CuO formation was only observed in the copper-riched catalyst after a NO_x lean reduction.

Studies of Grinsted et al.[90] and Budi et al. [91] suggested that dealuminum of Cu-zeolites are synonymous with the loss of cations exchange capacity, Brønsted acid sites and destruction of the geometry of copper ion sites. Moreover, dealumination of ZSM-5 was also observed by Petunchi and Hall[86], even in selective reduction in excess oxygen, particularly at high temperature. They suggested that the dealumination depends on conditions, particularly in a wet gas, the Si/Al ratio and the cation on the surface of zeolites[86]. The catalyst is more stable with increasing of Si/Al ratio, H₂O produced in the reaction probably caused the dealumination of catalysts. The order of the extent of dealumination of ZSM-5 catalysts is H-ZSM-5 > Cu-ZSM-5 > Na-ZSM-5[86]. Torre-Arbeu et al. [92] verified that Cu/ZSM-5 deactivation decreased when the copper content increased as well as when the zeolites Si/Al ratio increases, which agreed with the suggestion by Petunchi and Hall[86]. In addition, they found that Cu/H-ZSM-5 was more stable than Cu/Na-ZSM-5 because of Brønsted acid site(OH⁺) prevailing on surface of H-ZSM-5. From their TPO and TPR results, they consequently suggested that the cause of catalyst deactivation was mainly due to a change in copper species rather than in the MFI structure.

Loading some cations such as Le or Ce into Cu/ZSM-5 is believed to minimize the deactivation of the catalysts[93 - 95]. Le³⁺ ions prevent migration of Cu to the surface [93] and preserve the active Cu²⁺ species even under severe treatment [95].

For the influence of SO_2 on the SCR of NO over Cu/ZSM-5, it was found that SO_x did not inhibited the reaction and did not cause the deterioration of the catalyst [15,88,96]. The conversion of NO slightly decreased when SO_2 was added in the reactant feed.[15, 88].

From a study of destruction of the ZSM-5 structure using molecular dynamics and computer graphics methods, Ourni et al.[97] suggested that the mobility of SiO_2 - ZSM-5 increased with temperature increases. Also changes in the Si-O, Al-O and Cu-Al bond distance as well as in a pair of Si-O bond led to the destruction of Cu-ZSM-5.

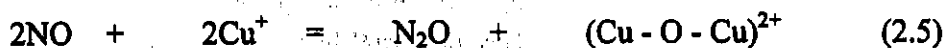
Temperature-programmed desorption (TPD), which is a crucial method for catalysis characterization has been investigated on Cu/ZSM-5. In the work of Li and Armor[98], NO was adsorbed on Cu/ZSM-5 at room temperature and TPD was then done. During the NO TPD, N_2O , NO and O_2 desorption peaks were detected. NO desorbed below 400 °C and most of the N_2O desorbed below 200 °C. They also noticed the NO disproportionated to N_2O and NO_2 at room temperature on Cu/ZSM-5 [99]. NO and O_2 TPD over Cu/ZSM-5 were also studied by Wang et al.[99]. The results of NO TPD indicated that about 80 % of copper sites are active for NO adsorption[99]. During NO TPD, NO partially desorbed below 300 °C, however, some NO reacted with extra lattice oxygen to form NO_2 and desorbed at around 400 °C and some oxygen was also formed and desorbed at the same temperature as NO_2 . In comparison, oxygen can adsorb on about 20 % of all copper ions. NO is considered to more strongly adsorbed on Cu/ZSM-5 than O_2 . Below 300 °C, oxygen was adsorbed mainly in molecular form, whereas the dissociative adsorption of oxygen happened above 300 °C[99].

Parrillo et al.[100,101] studied the TPD-TGA of isopropylamine over Cu ion exchanged zeolites. Physical adsorption-desorption on Cu/H-ZSM-5 occurred at low temperature(227 °C). Furthermore, isopropylamien ion formed on Brønsted acid site and decomposed to propylene and ammonia at 227-357 °C. Another desorption peak at high temperature (457 °C) corresponds to isopropylamine adsorb on a copper ion but not on an incorporated copper. From the TPD results, they suggested that the addition of copper decreases the concentration of Brønsted acid sites[100]. They also

studied propane TPD[100] and found that Cu-ZSM-5 can adsorb propane and desorb it as a propane molecule whereas H-ZSM-5 adsorbs propane but oligomerization occurred on the surface of the catalyst. In addition, Parrillo et al.[101] compared TPD of isopropylamine between Cu-Y and Cu-ZSM-5. They suggested that exchanged coppers are not stable on Y zeolite surface which is responsible for the huge differences in activity of NO reduction between Cu-Y and Cu-ZSM-5.

Satsuma et al.[102] used NH_3 -TPD to investigate acid properties of zeolites. They suggested that the acidity in the reduction of NO by hydrocarbons depends on the amount of acid in zeolites, but not the acid strength. However, they mentioned that acid properties of zeolites are not the major factor for selectivity in the SCR of NO. The NH_3 -TPD of H-ZSM-5 and Na-ZSM-5 was investigated by Chang et al.[103]. Temperatures of major TPD peaks of H-ZSM-5 are at 160 °C (vs), 260 °C(S), 400 °C (m) whereas peaks Na-ZSM-5 are at 140 °C(s) and 270 °C(m). They also applied O_2 - Temperature-Programmed isotope exchange between gas phase oxygen and lattice oxygen[103]. All zeolites (except H-ZSM-5 and H-ZSM-5) exhibited two types of isotope species Cu/Na-ZSM-5 and Cu/H-ZSM-5 while Na-ZSM-5 and H-ZSM-5 gave the same TPIE profile in which the formation of $\text{O}^{16}\text{O}^{18}$ increased linearly with temperature.

Transient study is a procedure which can be applied to identify the adsorption properties of gas species as well as the mechanism of a reaction. Transient behavior of NO decomposition over Cu/ZSM-5 was studied by Schay and Gucizi[104] and Pirone et al.[105]. In the NO pulses experiments of Schay and Gucizi[104], reversible poisoning of the catalyst by NO and O_2 was investigated. N_2 overshoot at the leading edge and O_2 peak at the tailing part of the pulse was also observed. They suggested that the rate of reaction was controlled by the desorption of O_2 which in turn was hindered by NO[104]. Pirone et al. [105] could detect the formation of N_2O during a transient phase after the pretreatment of zeolites. In contrast, N_2O was not observed from O_2 pretreated zeolite. Consequently, they suggested that the formation of N_2O is associated with the reoxidation as shown below



From gas switching experiments, Burch and Milling[53] found that the conversion of NO reached a steady-state activity in a very-short period of time. Cho [55] investigated role of O₂ and hydrocarbon in NO reduction, employing transient techniques. His results[55] indicated that the chromatographic separation effect among the reactant due to different adsorption affinity plays an important role in determining the catalytic activity of Cu-ZSM-5. Also, he showed that a cyclic operation between a lean and a rich condition was more effective than steady state operation for NO reduction by ethylene.

In the works of Centi and Perathoner[106] and Centi et al. [65], the overshoot of N₂O was also observed in unsteady state tests of the NO + O₂ reaction, but N₂O was not detected in NO decomposition. Since they found different trends of NO conversion in system with the different gas pretreatment and step changes to different gases in their transient experiments with NO + C₃H₈ + O₂ system, they suggested that products of NO reduction come from surface transformations of NO promoted by oxygen involving the decomposition of a N_xO_y species which they proposed to be the key intermediate in the reaction[65,106]. In the pretreatment with C₃H₈ + O₂ before doing experiment, partially oxidized species possibly form and block the adsorption of NO which may hinder NO reduction. NO may inhibit the reaction of C₃H₈ over both Cu/ZSM-5 and H-ZSM-5. In addition, from their kinetic studies[65], they found the NO concentration increases, the conversion of NO and C₃H₈ decrease until they become constants, On the other hand, NO conversion increased while hydrocarbon conversion decreased until both become constant with an enhancement of the C₃H₈ concentration.

The selective catalytic reduction of NO by C₂H₄ over Cu/ZSM-5 was studied by a pulse technique by Iwamoto and Takeda[64]. After the catalyst was saturated catalysts with C₂H₄, the NO + O₂ system produced more N₂ production than the NO system. Also, conversion to N₂ increased with increasing amounts of adsorbed C₂H₄. They, thus, classified adsorbed ethylene on Cu/ZSM-5 into two kinds of hydrocarbon

species. One is active for the reaction and the other is inert. The active species reacted with NO_x and O_2 to form a nitrogen-containing species and then into an isocyanite species. NO as well as NO_2 is directly included in the selective reduction as an active species.

Gaudin et al.[60] also studied effect of hydrocarbon pretreatments on transient de NO_x activity of Cu/ZSM-5 catalyst, a NO uptake can be observed without any formation of N_2 and CO . Propene was more efficient than propane. The reaction with pretreatment in hydrocarbon was better than the reaction without pretreatment but having hydrocarbon in feed. The nitrogen containing species are formed which are further decomposed into N_2 and CO_2 but found only in the presence of O_2 . In agreement with Kharas[45], they suggested that propene produces more coke deposits and is also more active than propane[60].

Cu-ZSM-5 typically prepared from copper ion-exchanged with either Cu-ZSM-5 or Na-ZSM-5 is called Cu/H-ZSM-5 and Cu/Na-ZSM-5 respectively. The differences of performance as well as characteristic of these two catalysts has been investigated. Campa et al.[107] studied NO decomposition over various copper loaded catalysts. They noticed that since the NO conversion from the reaction over Cu/H-ZSM-5 and Cu/Na-ZSM-5 fall on the same curve, the acid nature of zeolite has a minor role (if any) in the catalytic decomposition of NO . From the work of Engopasanan[108], a significant difference of activity between Cu/Na-ZSM-5 and $\text{Cu/NH}_4\text{-ZSM-5}$ in the reduction of NO by propane in the presence of excess oxygen was not observed. On the other hand, in the absence of oxygen, the NO conversion to N_2 on the $\text{Cu/NH}_4\text{-ZSM-5}$ was obviously more than on Cu/Na-ZSM-5 . Moreover, Torre-Abrev [92] found that, in the reduction of NO by propene, Cu/Na-ZSM-5 was more active than Cu/H-ZSM-5 . They also verified that Cu/ZSM-5 deactivation was higher on H-form zeolite compare to Na-form but decreased when the copper exchange level increased[92].

Furthermore, Chang et al.[103] noticed that both Cu/H-ZSM-5 and Cu/Na-ZSM-5 were very active for the oxidation of ethane with oxygen but not for the oxydehydrogenation of ethane.

Connection et al,[109] characterized the acidity of Na-ZSM-5, H-ZSM-5 and Cu/Na-ZSM-5 and Cu/H-ZSM-5 catalysts by using pyridine as a probe molecule. H-ZSM-5 was found to have both Lewis and Brønsted acidity with the Brønsted acid sites being both stronger and more numerous where as Na-ZSM-5 contain a mostly Lewis acidity, represented entirely by Na cations. Exchanging copper with H-ZSM-5 caused a large increase in Lewis acid sites, mainly represented by isolated Cu ions while the Brønsted acid sites were much decreased. Cu/Na-ZSM-5 had acid properties identical to those of Cu/H-ZSM-5. In addition, these sites found after heating either Cu/Na-ZSM-5 or Cu/H-ZSM-5 zeolite led to the decomposition of adsorbed pyridine and the formation of adsorbed ammonia probably by the Woffman gradation reaction. Also, the catalytic activity of both Cu/ZSM-5 catalysts for the reduction of nitrogen oxides was very similar.

From above paper review, a number of catalysts has been studied for the SCR of NO, however, among them, Cu/ZSM-5 is seem to be the most active and has been the most widely studied. The characterization and activity of Cu/ZSM-5 has been studied in much wide and deep detail in order to thoroughly understand in its efficient function on NO reduction by hydrocarbon. The understanding of the actual route and the mechanism of catalytic reduction of NO would bring about the development of higher performance catalyst to make this process to be possible in commercial.

Although Cu/ZSM-5 can be prepared by ion-exchanged Cu ion into either the Na- or H- forms of ZSM-5, the different performance of Cu/Na-ZSM-5 and Cu/H-ZSM-5 has been merely studied. It should be wealth studying the different activities between Cu/Na-ZSM-5 and Cu/H-ZSM-5. This would give us in more understanding in the role of the residual cations in Cu/ZSM-5. Consequently, it will be participate in the improvement of deNO_x catalyst.

To compare the different performance between Cu/Na-ZSM-5 and Cu/H-ZSM-5, characterizations and reaction studies would be performed. Many methods which have been used to characterize zeolites so far would be conducted in this study. Transient method would be used since it can study steady state, unsteady state and also adsorption behavior of the catalyst.