

CHAPTER II

LITERATURE REVIEWS

The removal of nitric oxide (NO) from flue gas has viewed considerable attention and has been studied. Several reaction mechanisms have been proposed. The best reaction to reduce NO is decomposition of NO without any reactants. However, this reaction does not proceed to any great extent. There are many offer reaction paths to reduce NO. This study investigates NO removal in the presence of hydrocarbons. The oxidation of NO to reactive NO₂ that then reacts with hydrocarbons was proposed to be the mechanism of Selective Catalytic Reduction (SCR) with CH₄ [15, 51-53]. Li et al. [54] and Sachtler et al. [55] also indicated that NO_x species could be bonded on zeolite Co²⁺ species and the formation of adsorbed NO₂ on Cu²⁺ sites is a rate determining step. Iwamoto et al. [56] reported the partial oxidation of hydrocarbon with O₂ to form an oxygenated hydrocarbon as intermediate, Kharas et al. [13] supported this mechanism as well. However, Ansell et al. [57] stipulated that the key intermediates are coke (formed on the zeolite) and NO₂ type species (formed on the exchanged copper sites). On the other hand, Inui et al. [58] presented a microscopic sequential reaction mechanism in which hydrocarbon reduce the surface of the catalysts and NO decomposed at the same time. Therefore, the mechanisms seem to depend on the type of catalysts and hydrocarbons used.

Iwamoto et al. [9, 10, 59-61] and Held et al. [62] found that a copper ion-exchanged MFI catalyst was active for NO removal by both direct NO decomposition and NO reduction. They showed that a small amount of hydrocarbons added in this process enhanced the catalytic activity of Cu/MFI in the presence of excess oxygen. Soon afterwards, Hamada et al. [25, 29, and 30] reported that protonated zeolite was active in the selective reduction of NO, but the required temperatures were much higher. Moreover, other metal ion-exchanged zeolites and relative materials have been investigated for nitric oxide removal. Concerning the influence of zeolite structure, Iwamoto et al. [11, 18, 63-65] showed that both MFI and mordenite structure were active. More recently, Hall et al. [66] found results similar to Iwamoto et al. and found that ferrierite structure (FER) could also be considered. The structure of a zeolite catalyst

appropriate for nitric oxide reaction seems to depend on the nature of hydrocarbon used. Li et al. [54] showed that the MFI structure was more favorable to the reduction of NO in the presence of C^{2+} hydrocarbons, while the FER structure was more favorable to the SCR with CH_4 . Hamada et al. [67] compared the catalytic activities of catalysts for NO decomposition. The order of activity was as follows; $Cu/MFI > Ag-Co_3O_4 > La-Sr-Co(Cu)-O > Pt/Al_2O_3 > Y-Ba-Cu-O/MgO$. In addition, among metal exchanged MFI zeolites studied, copper exchanged MFI zeolite was active for NO reduction at the low light-off temperature [63]. The order of active temperature regions of cation-exchanged MFI zeolites was $Cu(250^\circ C) < Co(350^\circ C) < H(400^\circ C) < Ag(450-600^\circ C) < Zn(600^\circ C)$. The influence of the preparation procedures on copper implanted in the zeolite is also of interest. Charjar et al. [68] studied the activity of Cu/MFI zeolites prepared according to three different procedures: exchange, impregnation and precipitation. The amount of C_3H_8 was used as a reductant and the oxygen content was higher than 0.5 vol%. The activities, measured as turnover frequencies, indicated the following order; $Cu/MFI(exchanged) > Cu/MFI(impregnated) > Cu/MFI(precipitated) > CuAl_2O_3$. Campa et al. [69] compared the activities for NO decomposition between copper ion-exchanged zeolite and copper impregnated MFI that was proposed by d'Itri and Sachtler [12]. They found that copper ion-exchanged zeolite promoted activity 10 times higher than copper impregnated one. This supported the idea that ion exchange is the best technique to prepare the catalyst. For ion-exchange method, the amount of metal used can be calculated from the equation [70] as described below;

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

The level of metal ion exchanged depends on the amount of aluminium ions in zeolite matrix. It was shown that the degree of exchange for the copper ion affects the activity for NO removal [11, 56, 70]. Iwamoto et al. [9, 71, 72] concluded that the repeated ion-exchange of MFI zeolite with Cu^{2+} solution resulted in excess loading of copper ions above 100% exchange level and the resulting catalysts were more active for NO decomposition. Cheung et al. [73] and Campa et al. [70] also agreed with this suggestion.

Nevertheless, a very important question is what is the effect of H₂O upon the reaction [21]. Most flue gas streams which contain NO_x also contain of a large amount of H₂O (2-18 mol%), hence H₂O tolerance is a crucial issue regarding a useful catalyst. The effect of steam on the activity of Cu/MFI for NO removal was reported especially under the high temperature condition. Martínez et al. [45] suggested that kinetic inhibition in either reversible or irreversible deactivation of Cu/MFI by the presence of H₂O in the feed during NO reduction. Addition of 2 mol% of H₂O in the feed retarded NO conversion reversibly. Unfortunately, Cu/MFI experienced a significant loss in its activity (60%) when it was operated at high temperature and in the presence of steam (650°C, 10%H₂O). From TPR characterisation not only the reduction band at 240°C (assigned to Cu²⁺ → Cu⁺) and at 350°C (assigned to Cu⁺ → Cu⁰) were found, but also the new bands at approximately 280 and 320°C were found for deactivated Cu/MFI. The band at 320°C was suggested as Cu species interacting with extraframework Al produced during dealumination of zeolite [46]. Additionally, the maximum temperature of the band assigned to Cu⁺ reduction shifted to higher temperatures after reaction with water vapour. The crystallinity of zeolite indicated by IR spectra between 400-1250 cm⁻¹ was not changed. Therefore, the main reason for the deactivation of Cu/MFI is the mobility of Cu²⁺ in the presence of H₂O rather than MFI dealumination. Abreu et al. [74] also supported the finding that no dealumination occurred but a change in copper species on Cu/MFI pretreated was found by adding 2 mol% H₂O. By using XRD, IR and ²⁷Al NMR spectra, high crystallinity of fresh and used catalysts were detected. According to the results of temperature programme desorption of NO, the used Cu/MFI catalysts presented a much smaller peak at low temperatures, representative of adsorbed NO, than the fresh one. Furthermore, H₂ TPR data indicated that the fresh and used Cu/MFI catalyst should have a different copper distribution. Kucherov et al. [75] concluded that the change in the local topology of the isolated Cu²⁺ sites is the predominant cause of the loss of catalytic activity of Cu/MFI after a high temperature treatment in the presence of steam. Steaming at 620°C or short calcination at 900°C did inhibit the chemisorption on the active sites and the reducibility of these sites [76]. These structural rearrangement happened before dealumination and agglomeration of the active metal. However, Tanabe et al. [47] reported dealumination caused the deactivation of Cu/MFI. Electron spin resonance (ESR) results indicated that aggregation of the copper ion did not

occur and copper remained as isolated copper ions in Cu/ZSM-5. The ESR spectra of dehydrated Cu/MFI suggested the migration of copper ions in the deactivated zeolite to other sites where gas molecules like nitric oxide and propene cannot reach them.

This migration is triggered by the dealumination of zeolite, and is shown in Figure 2.1 below.

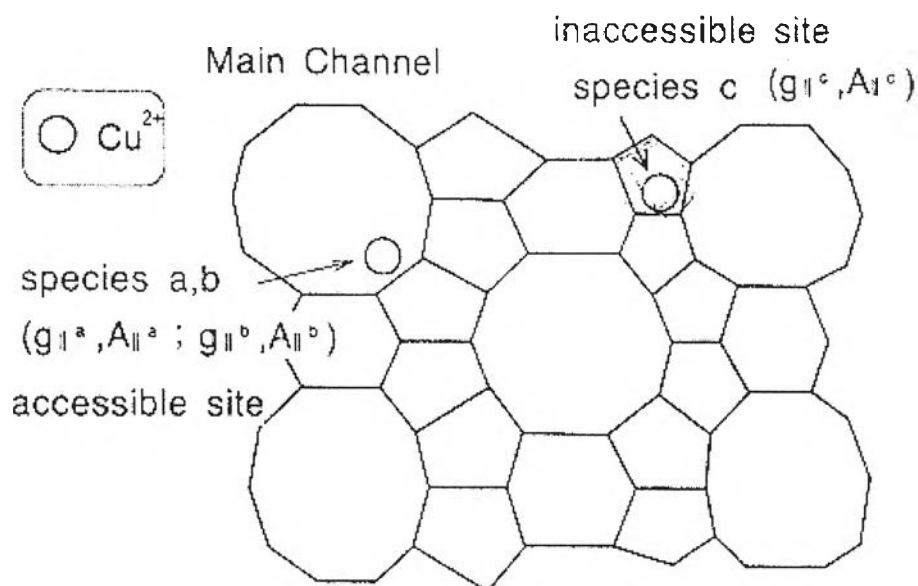


Figure 2.1 Schematic representation of the (100) face of MFI showing the 10-membered ring accessible to adsorbates and smaller 5-membered rings inaccessible to adsorbates. (Tanabe 1995 [47])

Matsumoto et al. [77] and Iwamoto et al. [78] also postulated that the hydrothermal treatment caused the Cu^{2+} species migration to another location in the MFI structure. Kharas et al. [44] reported that high temperature pretreatment at 600-800°C resulted in substantial deactivation on Cu/MFI. The higher the temperature, the more severe the deactivation. Cu/MFI loss micropore volume which was not caused by either coke deposition or dealumination but sintering of copper species to CuO and perhaps also to Cu_2O . On the other hand, Budi et al. [79] and Petunchi et al. [80] suggested that the aggregation of the transition metal component on the external surface of the zeolite was due to the dealumination of the zeolite framework. Accordingly, the instability of Cu/MFI in steam at higher temperatures severely limits its application in practical use.

Moreover, other metal species like Co, Mn or Ni [18-21, 30-34] exhibited high selectivity in the reduction of NO with methane. Under oxidizing conditions, Co/MFI zeolite is an active catalyst for reduction with methane, and the presence of nitrous oxide which is another source of air pollution. It was found to enhance the reduction of nitric oxide even in the absence of oxygen. Correa et al. [81] investigated decomposition of nitrous oxide in excess oxygen over Co- and Cu- exchanged MFI zeolites. They reported that Co/MFI was much more resistant than Cu/MFI in excess oxygen. The tolerance of Co/MFI catalysts to the excess oxygen is significant when Co^{2+} is stabilized in the zeolite framework.

Furthermore, Co/MFI is much more tolerant than Cu/MFI to wet exhaust streams containing N_2O and oxygen. Armor et al. [82] described the hydrothermal stability of Co/MFI comparing with Cu/MFI, MFI as protonated form and MFI as Na form at the condition of 2% H_2O at 750°C . By using XRD characterization, MFI as Na form transformed to cristobalite form indicating destruction of MFI structure while MFI as H form did not show any substantial loss in surface area, pore volume or Z-O_2 ($\text{Z} = \text{Si}$) under similar conditions. Although copper introduced into the zeolite framework impeded dealumination [83], Cu/MFI loss in surface area and micropore volume more severely than Co/MFI. By observing ^{29}Si and ^{27}Al NMR analysis, MFI as protonated form loss aluminium framework evidently with steaming supported by ref. 84. The dramatic increment of the octahedral non-framework aluminium on Cu/MFI was shown in steam condition. As for Co/MFI, while it was less active than Cu/MFI in the presence of steam at 500°C , it demonstrated a more stable performance for 18 h without further loss of activity upon return to the dry stream. Budi et al. [79] investigated hydrothermal-treatment on zeolite. The dealumination of zeolite lattice occurred to a lesser extent in the following; $\text{H/MFI} > \text{Cu/MFI} > \text{Co/MFI} > \text{Mn/MFI}$. Li et al. [85] reported the effect of steam on nitric oxide reduction by CH_4 in excess O_2 over Co/MFI. Not only nitric oxide reduction was inhibited by steam, but also CH_4 combustion. Burch and Scire [14] also examined the stability of Co/MFI under hydrothermal treatment and observed the dealumination of Co/MFI after pretreatment at 800°C and 114 torr of water for 24 h. On the other hand, platinum group metal catalysts have been studied for NO conversion. Iwamoto et al. [26] reported that platinum group metal has high resistance for the presence of steam even the a

large amount of H₂O in the feed gas. Moreover, modification by introduction of second cation on catalyst has also been studied. Kucherov et al. [86] and Rokosz et al. [87] studied the activity and stability of many kinds of metal (Ba, Ga, La, Ce, Co, Nb, Pd) implanted Cu/MFI. The addition of La proved to retard the high temperature rearrangement of Cu²⁺ sites especially the active square-planar Cu²⁺ configuration and dealumination [88]. Additionally, the two ingredient catalysts (Me/Cu/MFI) showed higher activity than Cu/MFI through conversion of NO to N₂ [89, 90]. The enhancement of catalytic activity of copper ion-exchanged Y type zeolite using the coexistence of Co³⁺ and Ni²⁺ was also observed [91]. Gucci et al. [92] established that the Co/NaY sample modified by platinum and ruthenium exhibited a superior behavior in methane activation. However, it is generally recognized that the ion-exchanged Al-silicate catalysts have a disadvantage in thermal and hydrothermal stability, owing to both the sintering of exchanged metal components and the dislocation of the aluminium from the zeolite framework and there are still the serious problems for the practical applications [93,94].

In order to overcome these difficulties, Inui et al. synthesised silicate crystals (metallo-silicates) by isomorphous substitution of aluminium in MFI for other transition metal elements at the stage of gel formation before crystallization [95-97]. For example, H-Fe-silicate containing a higher amount of iron showed a higher activity in light olefin conversion to gasoline range hydrocarbons [98, 99]. Inui et al. [100-102] applied H-Cu-silicate for decomposition of NO relative to Cu/MFI. The catalytic performance of both catalysts was evaluated by decomposition of NO in the absence of oxygen. The NO conversion at steady state for Cu/MFI and H-Cu-silicate were 42% and 12%, respectively. It seems to be an advantage of Cu/MFI, however, the position of Cu is not in the framework but in the pore channels. Therefore, this kind of Cu is not stable and the copper is easily sintered or evaporated when it is placed under high temperature conditions or under repeated redox cycles. It can be suggested that metallosilicate catalysts having an MFI structure show higher thermal stability than ion-exchanged MFI [49]. By studying Co incorporated MFI catalyst (H-Co-silicate) comparing with Co exchanged MFI (Co/MFI) and Fe incorporated MFI catalyst (H-Fe-silicate) comparing with Fe exchanged MFI (Fe/MFI), the performance for NO removal of metal incorporated MFI remained higher NO conversion even after thermal treatment than metal exchanged MFI catalyst. Although a

part of metal component might be sintered and migrated in H-Me-silicate, most of them were still highly dispersed to give high NO conversion in contrast with Me/MFI. Moreover, many types of metallosilicates (Ni, Mn, Co, Ga) were investigated as well [103]. H-Co-silicate was active to combust hydrocarbons moderately enhancing more chance for hydrocarbons to be used for NO removal suitably as shown in Table.2.1. To study the stability of H-Co-silicate, the effect of coexistence of steam, CO₂ and SO₂ on the catalyst performance was examined in ref. 48. It was found that water vapour retarded the hydrocarbon conversion to CO₂ but no effect was observed on NO conversion. Therefore, the addition of CO₂ and SO₂ did not affect the reaction for NO removal directly. Furthermore, catalytic properties of H-Co-silicate for both hydrocarbon and nitric oxide conversions were significantly increased by a high temperature calcination in air stream including steam [104]. This is of interest for the increment of the activity for NO removal of H-Co-silicate catalyst. However, no study mentions the optimum condition to promote high activity for NO conversion without any deactivation. Accordingly, the objectives of this study concern the activity of catalysts applied for NO removal under severe condition. The main catalysts investigated were copper exchanged MFI (Cu/MFI), Co incorporated MFI (H-Co-silicate), Cu exchanged Co incorporated silicate (Cu/Co-silicate). Palladium exchanged copper exchanged MFI (Pd/Cu/MFI) was also studied.

Table 2.1 Maximum NO conversion on various metallosilicates (Inui 1994 [103])

Metallosilicate catalysts					Maximum data of NO conv. (%)				
Cat.No.	Kind of metal	Acidity ^c	Redox ^d property	Activity for hydrocarbon	Temp. (°C)	NO conv. (%)	Conversion of cetane (%)		
							to CO ₂	to CO	to(CO ₂ +CO)
Cat.1	None ^a	+	-	+	450	14.9	17	39	56
Cat.2	Al	+++++	-	+	600	27.1	53	47	100
Cat.3	Ga	+++++	+	+	600	55.5	41	40	81
Cat.4	Fe	+++	+++	++++	250	22.3	32	10	42
Cat.5	Co	++	++	+++	400	61.6	53	14	67
Cat.6	Ni	++	+++	+++	380	48.9	74	10	84
Cat.7	Mn	+	+++	+++	350	23.0	56	13	69
Cat.8	Cu ^b	+	+++++	++++	300	22.3	57	10	67

Content of metal Si/Me = 20, NO 1000 ppm, cetane 560 ppm, O₂ 10.0%, N₂ diluted, SV = 30000 h⁻¹,

^a Si/Me = ca.5000.

^b Si/Cu = 185.

^c Estimated by NH₃ TPD measurements, the unit is amount of NH₃ adsorbed per unit catalyst weight.

^d Estimated by weight decrease by hydrogen reduction and oxygen uptake using thermogravimetric analyzer, the unit is weight decrease or gain per unit catalyst weight.

^e Compared by oxygen excess condition using cetane as the hydrocarbon, the unit is amount of hydrocarbon converted per unit catalyst volume and unit time.

The objectives of this study

1. To study the effect of severe conditions on the activity of NO conversion of Cu/MFI, H-Co-silicate.
2. Determine the optimum conditions of H-Co-silicate to promote high NO conversion.
3. To prepare Cu/Co-silicate and compare its activity with that of Cu/MFI and H-Co-silicate in severe condition.
4. To characterize the catalyst by using many techniques in both physical and chemical method.
5. To improve the activity of Cu/MFI in severe condition by addition of Pd metal that is resistant to hydrothermal condition.

Scope of work

1. Preparation of Cu/MFI, H-Co-silicate, Cu/Co-silicate, Pd/Cu/MFI and Pd/MFI.
2. Pretreatment of catalysts using
 - 2.1 Hydro-treatment condition in the range of 0-10% H₂O
 - 2.2 Thermal-treatment condition between 600-1100°C
 - 2.3 Hydrothermal-treatment condition up to 1000°C with 10% H₂O
3. Characterizations of catalyst by
 - 3.1 surface area by BET method
 - 3.2 bulk composition by Inductively coupled plasma (ICP) method
 - 3.3 crystallinity of sample by X-ray diffraction (XRD) or Infrared (IR) characterization
 - 3.4 morphology on the surface of sample by Scanning Electron Microscopy (SEM) method
 - 3.5 the coordination of Si in the framework of zeolite by ²⁹Si Magnetic Angle Spinning Nuclear Magnetic Resonance (²⁹Si MAS NMR) analysis
 - 3.6 high spin Co²⁺ and Cu²⁺ of catalyst by Electron Spinning Resonance (ESR) analysis
 - 3.7 cobalt species of catalyst by UV-Vis method

- 3.8 acidity by In situ Fourier Transform Infrared (In situ FTIR) analysis using pyridine as a probe molecule
- 3.9 the reducibility of catalyst by Temperature Programmed Reduction of H₂ (H₂ TPR) method
- 3.10 the decomposition of NO using NO 1,000 ppm, He balance with a GHSV of 30,000h⁻¹. The reaction was carried out between 200 and 600°C.
4. Reaction test using feed gas compositions of NO 1,000 ppm, n-C₈H₁₈ 1,000 ppm, O₂ 2mol%, He balance with a GHSV of 30,000 h⁻¹. The reaction was carried out between 200 and 600°C.
5. Stability test using feed gas compositions of NO 1,000 ppm, n-C₈H₁₈ 1,000 ppm, O₂ 2mol%, H₂O (0 and 10mol%), He balance with 30000 h⁻¹. This reaction was investigated at 400°C for 9 h.