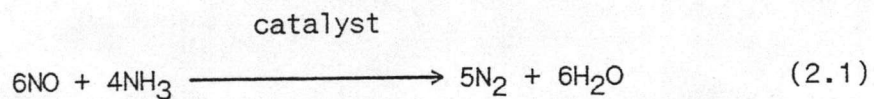


CHAPTER II

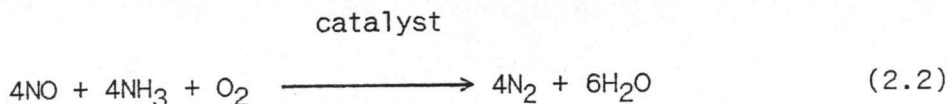
THEORY

2.1 The concept of reduction of nitric oxide with ammonia

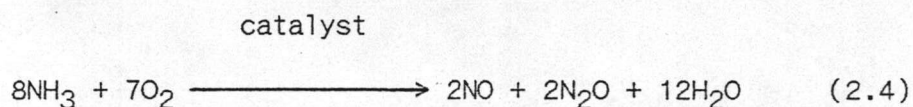
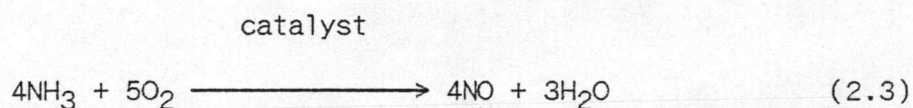
With the effect on human health from nitric oxide, NO, control techniques have been developed and implemented to reduce the emission by a significant amount for a variety of source fuel combustions, notably in the utility boiler sector. One of the most promising processes to remove nitric oxide from exhaust gas is the selective catalytic reduction technique. This technique reduces NO to N₂ and H₂O with injection of NH₃. The reaction is described as;



To improve percentage of NO conversion, O₂ is added to the reaction and the reaction is allowed to take place at condition with the catalyst. The reaction of N₂-NH₃-O₂ is described as;



The catalyst for this application should provide sufficient intrinsic activity to the conversion of 50–90 % , high resistance to deactivation, high selectivity to avoid the undesired reaction of ammonia with excessive oxygen. In addition, in the presence of O_2 and high temperature, the combustion of NH_3 with O_2 can occur as the set of reactions below;



Thus, the suitable condition of the catalytic reduction of NO with NH_3 in the presence of O_2 should be taken under the low reaction temperature.

2.2.1 Thermodynamical consideration for the reaction of NO-NH₃-O₂ system

As discussed previously, the stoichiometric reaction can be written on some conditions of various experiments, but it does not show the possibility of the reaction intended to represent the system of NO-NH₃-O₂. To determine whether a reaction described by a stoichiometric relation is possible it is necessary to rely on thermodynamics, and particularly on the data of Gibbs free energy, $(\Delta G_R^0)_T$.

The greater the decrease in $(\Delta G_R^0)_T$ accompanying a reaction, the more the reaction is favoured. In dealing with a single stoichiometric equation:

$$\sum v_i A_i = 0 \quad (2.5)$$

where A_i = chemical compound i in reaction

v_i = stoichiometric coefficient of compound i

the variation in standard Gibbs free energy reaction at temperature T = (standard Gibbs free energy of the products) - (standard Gibbs free energy of the reactants) is expressed by :

$$(\Delta G_R^0)_T = \sum_{i=1}^S v_i [(\Delta G_f^0)(A_i)]_T \quad (2.6)$$

in joules, J , for v_i moles of A_i .

where $[(\Delta G_f^0)(A_i)]_T$ is the variation in standard Gibbs free energy of formation of compound A_i at temperature T .

It is very difficult to compute the value of $[(\Delta G_f^0)(A_i)]_T$ directly, while it is easy to determine or to estimate :

$$[(\Delta G_f^0)(A_i)]_{T_0} , [(\Delta H_f^0)(A_i)]_{T_0}$$

and the values of $C_p^0(A_i)$ as a function of temperature.

The most widely used reference temperature T_0 is 298 K. This makes it possible to calculate $(\Delta G_R^\circ)_T$:

$$\begin{aligned}
 (\Delta G_R^\circ)_T &= (\Delta H_R^\circ)_{298K} - T(\Delta S_R^\circ)_{298K} + \int_{298}^T \sum v_i C_p^\circ(A_i) dT \\
 &+ T \left(\int_{298}^T \sum v_i C_p^\circ(A_i) \frac{dT}{T} \right) \quad (2.7)
 \end{aligned}$$

which can often be simplified to

$$(\Delta G_R^\circ)_T = (\Delta H_R^\circ)_{298K} - T(\Delta S_R^\circ)_{298K} \quad (2.8)$$

provided $\sum v_i C_p^\circ(A_i)$ is small.

One of the reactions of NO-NH₃-O₂ system is calculated for the variation in standard Gibb's free energy which accompanies the reaction below by using equation (2.7) and (2.8)



in the gas phase, at 473 K and atmospheric pressure, and knowing that:

$(\Delta H_f^\circ)_{298}$ (NO)	=	90000	J/mole
$(\Delta H_f^\circ)_{298}$ (NH ₃)	=	-46000	J/mole
$(\Delta H_f^\circ)_{298}$ (H ₂ O)	=	242000	J/mole
$(\Delta G_f^\circ)_{298}$ (NO)	=	87000	J/mole
$(\Delta G_f^\circ)_{298}$ (H ₂ O)	=	-229000	J/mole
$(\Delta G_f^\circ)_{298}$ (NH ₃)	=	-16000	J/mole
$(\Delta H_f^\circ)_{298}$ (O ₂ element)	=	0	at all temperatures
$(\Delta H_f^\circ)_{298}$ (N ₂ element)	=	0	at all temperatures
$(\Delta G_f^\circ)_{298}$ (O ₂ element)	=	0	at all temperatures
$(\Delta G_f^\circ)_{298}$ (N ₂ element)	=	0	at all temperatures

First calculation step :

$$\begin{aligned} (\Delta H_R^\circ)_{298K} &= 6(-242000) - 4(90000) - 4(-46000) \\ &= -1628000 \quad \text{J} \end{aligned}$$

Followed by,

$$\begin{aligned} (\Delta G_R^\circ)_{298K} &= 6(-229000) - 4(87000) - 4(-16000) \\ &= -1658000 \quad \text{J} \end{aligned}$$

and

$$\begin{aligned} (\Delta S_R^\circ)_{298K} &= \frac{(\Delta H_R^\circ)_{298K} - (\Delta G_R^\circ)_{298K}}{298} \\ &= \frac{(-1628000) - (-1658000)}{298} \\ &= 100.67 \quad \text{J/K} \end{aligned}$$

Then calculate;

$$\begin{aligned}
 (\Delta G_R^0)_{473K} &= (-1628000) - (473)(100.67) + \\
 &\int_{298}^{473} [29.60 - 11.2416 \times 10^{-2}T - 6.9124 \times 10^{-5}T^2] dT + \\
 &473 \left(\int_{298}^{473} [29.60 - 11.2416 \times 10^{-2}T - 6.9124 \times 10^{-5}T^2] \frac{dT}{T} \right)
 \end{aligned}$$

The result is;

$$\begin{aligned}
 (\Delta G_R^0)_{473} &= -1685104 \text{ J} \\
 &= -1685.104 \text{ kJ}
 \end{aligned}$$

The values of $C_p^0(A_i)$ as a function of temperature are shown in table below and the simplified expression is;

$$C_p^0(A_i) = a + bT + cT^2 \quad [\text{J/mole.K}] \quad (2.9)$$

component A_i	a	$bx10^2$	$cx10^5$
4 NO	4x29.50	4x0.8188	-4x0.2925
4 NH ₃	4x35.15	4x2.9540	4x0.4421
O ₂	29.10	1.1580	-0.6076
4 N ₂	4x29.00	4x0.2199	-4x2.8710
6 H ₂ O	6x33.46	6x0.6880	6x0.7604
$\sum v_i C_p^0(A_i)$	29.06	-11.2416	-6.9124

The result from the calculation of other NO-NH₃-O₂ reaction is tabulated in Table 2.1. From the values of $(\Delta G_R^0)_T$ at various temperatures, it indicates as far as the main initial reaction is concerned, that the first reaction is more favourable to occur than the second reaction. Considering the fifth and the sixth reactions, NO₂ can be reduced by reacting with NH₃ which is confirmed by the negative values of $(\Delta G_R^0)_T$. Besides, the presence of NO₂ increases the negative values of $(\Delta G_R^0)_T$ of the second reaction as expressed in the eighth reaction but decreases the negative values of $(\Delta G_R^0)_T$ of the first reaction as expressed in the seventh reaction. This effect shows that the eighth reaction tends to favourably occur comparing to the seventh.

However, NO₂ is not a gaseous reactant in this research and the values of $(\Delta G_R^0)_T$ of the third reaction shows that the oxidation of NO with O₂ is unfavorable to occur. Moreover, the values of $(\Delta G_R^0)_T$ of the disproportionation of NO to produce NO₂ expressed in the fourth reaction gives the same meaning. For the combustion of NH₃, this reaction is favourable to occur in the presence of O₂ which is confirmed by the values of $(\Delta G_R^0)_T$ of the ninth, the tenth, and the eleventh reaction. As a consequence, the addition of O₂ into the reaction of NO-NH₃ (the second reaction in Table 2.1) should be controlled as small amount in order to maintain NH₃ for reacting with NO. To enhance the conversion of NO, catalyst is necessary for the NO-NH₃ reaction in the presence of O₂ which can readily attract NO as NO₂ species and suppress the combustion of NH₃ at the temperature range of 100-300 °C.

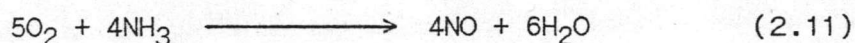
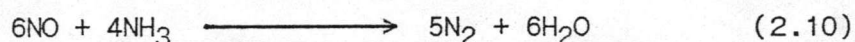
Table 2.1 Calculation result of Gibbs Free Energy of Reaction of NO-NH₃-O₂ System at Various Temperatures

Reaction	Gibbs Free Energy, (ΔG_R^0) _T , kJ				
	25 °C	100 °C	200 °C	300 °C	400 °C
1. $6\text{NO} + 4\text{NH}_3 \text{ ----> } 5\text{N}_2 + 6\text{H}_2\text{O}$	-1832.00	-1841.43	-1858.02	-1879.77	-1907.28
2. $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \text{ ----> } 4\text{N}_2 + 6\text{H}_2\text{O}$	-1658.00	-1668.14	-1685.10	-1706.45	-1732.64
3. $2\text{NO} + \text{O}_2 \text{ ----> } 2\text{NO}_2$	-72.00	-61.55	-47.14	-32.34	-17.29
4. $3\text{NO} \text{ ----> } \text{N}_2\text{O} + \text{NO}_2$	-107.00	-215.22	-231.19	-246.89	-262.49
5. $6\text{NO}_2 + 8\text{NH}_3 \text{ ----> } 7\text{N}_2 + 6\text{H}_2\text{O}$	-2726.00	-3126.61	-3674.44	-4237.24	-4814.73
6. $2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 \text{ ----> } 3\text{N}_2 + 6\text{H}_2\text{O}$	-1412.00	-1432.91	-1463.76	-1498.35	-1536.81
7. $\text{NO} + \text{NO}_2 + 2\text{NH}_3 \text{ ----> } 2\text{N}_2 + 3\text{H}_2\text{O}$	-793.00	-803.12	-818.36	-835.86	-855.76
8. $6\text{NO} + 2\text{NO}_2 + 8\text{NH}_3 + 7\text{O}_2 \text{ ----> } 8\text{N}_2 + 12\text{H}_2\text{O}$	-3004.00	-3093.56	-3220.14	-3355.62	-3500.74
9. $4\text{NH}_3 + 3\text{O}_2 \text{ ----> } 2\text{N}_2 + 6\text{H}_2\text{O}$	-1310.00	-1321.57	-1339.28	-1359.83	-1383.36
10. $4\text{NH}_3 + 5\text{O}_2 \text{ ----> } 4\text{NO} + 6\text{H}_2\text{O}$	-962.00	-974.92	-993.37	-1013.08	-1033.95
11. $8\text{NH}_3 + 7\text{O}_2 \text{ ----> } 2\text{N}_2\text{O} + 2\text{N}_2 + 12\text{H}_2\text{O}$	-2414.00	-2455.54	-2519.87	-2593.52	-2675.61
12. $8\text{NO} + 2\text{NH}_3 \text{ ----> } 5\text{N}_2\text{O} + 3\text{H}_2\text{O}$	-836.00	-1078.06	-1112.27	-1146.06	-1179.84

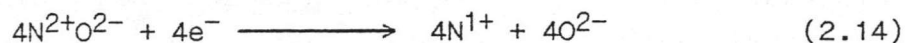
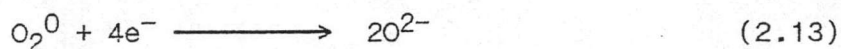
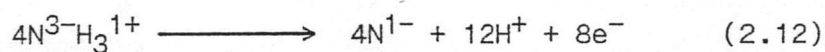
2.1.2 Role of catalyst in NO-NH₃-O₂ reaction

From reaction (2.2), catalyst is necessary in the reaction of NO-NH₃-O₂ which takes place at low temperature and increases rate of reaction. This section will describe the role of catalyst in reaction of NO-NH₃-O₂.

Though several reactions between NO and NH₃, with the excessive O₂ are chemically possible, the two primary interests are usually written as;



The catalyst is required to catalyze the first reaction very selectively whereas avoiding or at least minimizing the second. For the reaction (2.2), N₂ and H₂O are the obtained products. It indicated that the electrons had been transferred between reactants in the reaction. The characteristic of electron transfer may be written as ;



From electron transfer characteristic, the $\text{NO-NH}_3\text{-O}_2$ reaction is the redox one. Noble-metals (such as Pt, Pd, Ag) are suitable to be used as active metal catalyst for this reaction, because they are resistant to self oxidation to a pure metal at the relevant temperature and they are capable of chemisorbing oxygen. Table 2.2 shows classification of metal and their ability in chemisorbing.

Table 2.2 Classification of metal according to their abilities in chemisorbing

Group	Metals	Gases						
		O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
A	Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os	+	+	+	+	+	+	+
B_1	Ni, Co	+	+	+	+	+	+	-
B_2	Rh, Pd, Pt, Ir	+	+	+	+	+	-	-
B_3	Mn, Cu	+	+	+	+	±	-	-
C	Al, Au	+	+	+	+	-	-	-
D	Li, Na, K	+	+	-	-	-	-	-
E	Mg, Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi	+	-	-	-	-	-	-

(+ means that strong chemisorption occurs; ± means that it is weak; - means unobservable.)

Source : Bond, G.C. Heterogeneous Catalyst: Principle and Application.
Oxford University Press, Ely House, London W.1, 1974, pp.22

Considering the mechanism, there are two interesting aspects of mechanism of $\text{NO-NH}_3\text{-O}_2$ reaction. Firstly, oxygen is the first species which adsorbs on the surface of catalyst called oxygen surface. Next, NO absorption occurs on oxygen surface as NO_2 -like species, one oxygen of which comes from NO and the other comes from oxygen surface. At the same time, NH_3 adsorb on oxygen surfaces. After

that N_2 and H_2O which have been produced from the reaction of $NO-NH_3-O_2$ are carried out from surface of catalyst at relevant temperature. This aspect was proposed by Niiyama et al. (1980) using Cr_2O_3 as a catalyst. This mechanism is illustrated as uncomplete scheme in Figure 2.1.

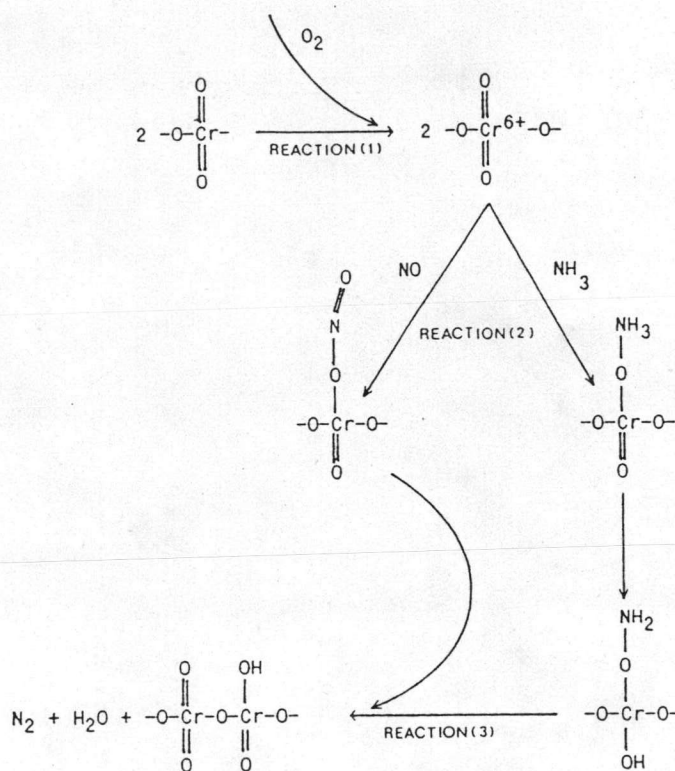


Figure 2.1 Uncomplete mechanism of $NO-NH_3$ reaction on the Cr_2O_3 catalyst in the presence of O_2

Secondly, NH_3 is the first species which adsorbs on surface of catalyst. After that, NO adsorbs over adsorbed- NH_3 and then at suitable temperature, N_2 and H_2O can be produced. Eventually, the reduced catalyst is oxidized by O_2 to reproduce the previous property before $NO-NH_3$ reaction. This aspect was proposed by the work of Inomata et al. (1980) using V_2O_5 as a catalyst. This mechanism is shown in Figure 2.2.

In this work, two types of catalyst were used. The first is cation-exchanged zeolite which is composed of Pt-HY and Cu-Pt-HY. For zeolite, it has been known that a non-ionic molecule is oxidized easily in cavities of a zeolite. Moreover, Pt is selected as exchanged cation by the reason that transition metal ions have the ability to change valence state easily and can therefore function as an intermediate storage for electrons that are needed in the reaction. These properties are useful to oxidize NO to NO₂ as the active species which can react with NH₃ to produce N₂ and H₂O. However, Pt easily reduces itself in the presence of oxygen at high temperature. Cu is capable of the adsorption of oxygen especially in the condition with very dilute concentration. So, Cu is loaded to Pt-Zeolite to decrease the reduction of Pt and improved activity of catalyst. The last one is vanadium pentoxide, V₂O₅, which is supported on titanium dioxide, TiO₂. V₂O₅ catalyst is used in practice as one of the best catalysts for the NO-NH₃ reaction, because of its high activity at lower temperature and high resistance to the poisoning by SO_x. Furthermore, under the dilute gas condition, it is well known that the rate of reaction on vanadium oxide catalyst must be accelerated by the addition of O₂.

2.2 Literature survey

Many studies have been done on the reaction of NO and NH₃. Selective catalytic reduction (SCR) of NO and NH₃ has become the most widely applied method and in 1983 over 150 commercial SCR plants were in operation. In this section, the studies of the reaction between NO and NH₃ over cation exchanged zeolite and V₂O₅ catalyst are presented.

Otto, Shelef and Kummer (1970) investigated the catalytic interaction between NO and NH₃. They studied the detail of the this reaction by circulating mixture of isotopic label of ¹⁵NH₃ and ¹⁴NO, and Ar in a gradientless batch reactor over sample of Pt supported on alumina. They found that nitrogen was formed predominantly from the interaction of one molecule of NH₃ and one molecule of NO, while nitrous oxide, N₂O, in contrast, was formed mainly by the interaction of a pair of NO molecules. This is an important evidence because it confirms that NH₃ is necessary in the reaction as NO reduction.

Mizomoto, Yamazoe and Seiyama (1982) studied the catalytic reduction of NO by NH₃ over Cu²⁺ ion-exchanged Y-type zeolites, (Cu²⁺-NaY). The isotopic tracer studies were examined as well as relevant studies on the transient reaction of reduced catalysts. They found that N₂ was mainly formed by bimolecular reaction between NO and NH₃, while the nitrogen atom of nitrous oxide came solely from NO. These results support the work of Otto et al. (1970).

Seiyama, Arakawa, Matsuda, Takuita and Yamazoe (1977) studied the catalytic reduction of NO by NH₃ over transition metal ion exchanged Y zeolites, (Me-Y). Among various catalysts used, they found that Cu²⁺-Y was particularly interesting, exhibiting low temperature activity coupled with an unusual activity temperature profile. Moreover, they investigated the effect of binary metal ion exchanged system. Cu²⁺ was selected as the first component whereas the second component such as Pd, Ni, Fe, and Co were varied. The results showed that conversion of NO was relatively increased.

This study is important because it indicates that Cu(II) can promote the activity of NO-NH₃ reaction to get a high conversion of NO.

Inomata, Miyamoto and Murakami (1980) investigated the mechanism of the NO and NH₃ on vanadium oxide catalyst. The reaction was conducted under the dilute gas condition in the presence of O₂. They found that NH₃ was strongly adsorbed adjacent to V⁵⁺=O as NH₄⁺ on the surface of V₂O₅ catalyst whereas NO was hardly adsorbed. Then, a gaseous NO is reacted with the adsorbed NH₃, i.e., NH₄⁺(ad), to form N₂, H₂O, and V-OH. The V-OH species were reoxidized to V⁵⁺=O by either gaseous O₂ or bulk V⁵⁺=O species. These results are important because the role of O₂ in the reaction of NO-NH₃ was verified.

Niiyama, Sasamoto, Yoshida and Echigoya (1981) studied the role of oxygen in NO-NH₃-O₂ reaction system at low concentration of NO and NH₃ (500 ppm) by transient response technique. They used CuSO₄-Activated Carbon as a catalyst. From the experimental results, they found that the conversion of NO was very low in the absence of O₂. These results confirm the work of Inomata et al. (1980) that O₂ participates in the reaction.

Baiker, Dollenmeier and Glinski (1987) investigated the efficiency of titania supported vanadium oxide as catalysts for selective catalytic reduction (SCR) of NO by NH₃. The reaction was performed in a continuous tubular fixed-bed microreactor. They found that high activity on the conversion of NO was obtained by three- and four-fold impregnations of vanadium oxide on titania. They

explained the enhanced activity on NO conversion after several impregnations of vanadium oxide by the High Resolution Electron Microscopy result. The results showed that vanadia were preferentially deposited at the edges of titania and that even after several impregnations the amorphous vanadia did not form a compact layer. So, the structure of vanadium oxide was disordered or defective which gave higher activity on the conversion of NO than crystalline vanadium oxide.

From literature survey, catalysts such as V_2O_5 and cation exchanged zeolite were used in the catalytic reduction of NO by NH_3 . The results of many experiments show that the conversion of NO is enhanced by these catalysts. However, there are two interesting questions about these catalysts on the conversion of NO that do not investigate by these researchers in the case as follow. Firstly, how does the efficiency of NO conversion change when V_2O_5 content is varied on TiO_2 comparing to pure V_2O_5 . Secondly, how does the efficiency of NO conversion change when Cu(II) is loaded to Pt-HY comparing to Pt-HY. Therefore, one of the objectives of this work is to try to find out the solution for the above two questions.