CHAPTER III

THEORY

The selective catalytic reduction (SCR) of NO_x with ammonia by V_2O_5/TiO_2 catalyst has been extensively employed in industrial process for controlling the pollution due to nitrogen oxide gases from stationary source. In this chapter, an attempt is made to describe the principle of catalytic combustion, formation of NO_x and reduction of NO_x by catalyst technology. In addition, titanium oxide supported vanadium oxide catalyst is mentioned later in section 3.4.

3.1 Principle of catalytic combustion [30]

The objective of introducing a catalyst in the combustor is to carry out heterogeneous oxidation on the surface of the catalyst. By choice of a suitable catalyst, one can ensure that the activation energy for the heterogeneous reaction is much lower than that for the purely homogeneous case. Consequently, appreciable heterogeneous oxidation rate can be achieved for temperatures and fuel concentration much lower than those require for the homogeneous reactions to proceed. Because of this, and also due to the large thermal inertia of the bed, catalytic combustors can sustain stable combustion at fuel concentrations much below those possible in conventional combustors.
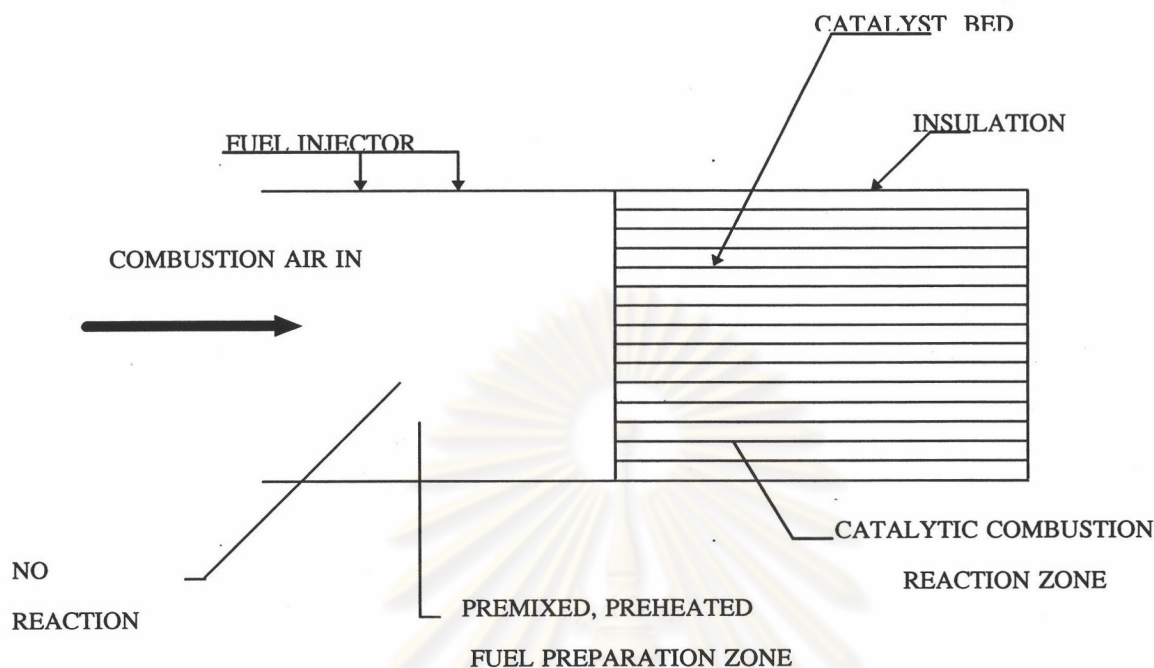
CATALYST BED

INSULATION

FUEL INJECTOR

COMBUSTION AIR IN

NO
REACTION

PREMIXED, PREHEATED
FUEL PREPARATION ZONE

CATALYTIC COMBUSTION
REACTION ZONE

Figure 3.1 Diagram of the catalytic combustor [30]

From Figure 3.1, the catalytic combustor consists of a catalyst bed through which a premixed and preheated fuel/air mixture is passed. In the first part of the bed, where the catalyst temperature is low, the reaction is "kinetically controlled" and the rate of overall process is controlled by the intrinsic surface kinetics. Thus, in a catalytic combustor, the combustion process is initiated and stabilized by the catalytic substrate.

The surface reaction coupled with the large thermal inertia of the bed, enables catalytic combustors to carry out stable, highly efficient (99.9%) combustion over a wide range of equivalence ratios.

3.2 Formation of NO_x [1]

The main sources of NO_x in the lower atmosphere are the combustion of fossil fuels and the burning of biomass (only partly caused by forest fires initiated by natural causes). Other sources are nitrogen fixation by lighting, volcanic activity, the oxidation of ammonia in the troposphere, the inflow of NO from the stratosphere, the oxidation of atmospheric nitrogen at high temperature, and ammonia oxidation from the decomposition of proteins.

Road and air traffic as well as other industrial and domestic burning of fossil fuels, are thus the most important sources of oxides of nitrogen. Traffic is responsible for the major part in the industrialized countries. For a selection of industrialized countries mobile sources contribute to 40-60% of the total NO_x emission. The overwhelming sources of N_2O in the atmosphere of the earth is microbiological. The N_2O, occurring at levels of about 500 mg/m^3 is produce by denitrification process.

The main sink for nitrogen oxides occurs via chemical process, involving oxidation reactions with OH radicals and ozone, to form HNO_3 and peroxy acetyl nitrate (PAN).

The pollutants from power plants, industrial boilers and stationary engines consist mainly of particulates, sulphur oxides and nitrogen oxides. The existence of seven oxides of nitrogen is known, NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5.

However, the combustion gas resulting from fossil fuel consists mainly of the oxides NO and NO_2, with in the form of nitric oxide (NO) with the residual, usually less than 5%, in the form of nitrogen dioxide (NO_2). The kinetics of NO_x formation from both atmospheric and fuel nitrogen are reasonably well understood for homogeneous reactions, such as those present in flame. However, virtually no information is available regarding the kinetics of oxidation or reduction of nitrogenous species on the surface of catalysts used in catalytic combustion. Nevertheless, it is important to note that recent research indicates that surface catalytic reactions could significantly influence the oxidation of fuel-bond nitrogen.

Three types of NO_x can be distinguished in flue-gas:

thermal NO_x : formed by fixation of atmospheric nitrogen ;

fuel NO_x   : formed by the oxidation of the nitrogen-containing compounds in the fuel ;

prompt NO_x : formed by the oxidation of intermediate HCN.

3.2.1 Thermal NO_x : The formation of this type is fully explained by the mechanism proposed by Zeldovich. [31]

$$O_2 \ + \ N_2 \ \rightleftarrows \ NO \ + \ N \qquad (3.1)$$

$$N \ + \ O_2 \ \rightleftarrows \ NO \ + \ O_2 \qquad (3.2)$$

For the formation of NO from N_2 and O_2 in (1)+(2), the reaction rate was determined as

$$d[NO]/dt = 9*10^{14} \exp(-68180/T)*[NO]*[O_2]^{0.5}$$

The fixation of atmospheric nitrogen is thus sensitive to temperate. In cool flames, the formation of thermal NO_x is lower. In addition to this mechanism, the following reaction occurs in fuelrich flames :

$$N \quad + \quad OH \quad \rightleftharpoons \quad NO \quad + \quad H \qquad (3.3)$$

3.2.2   Fuel NO_x : This is formed from the gas-phase oxidation of devolatilized fuel nitrogen, and from the heterogeneous oxidation of char nitrogen in the flame tail. Fuel NO_x formation is independent of the temperature of the flame at the normal combustion temperature and is insensitive is to the nature of the organic nitrogen compound. According to the Fenimore [32] mechanism, the organic nitrogen compounds from a complex which can be attacked by OH-radicals and NO molecules, in the reactions :

$$N\text{-complex} \quad + \quad OH \quad \rightleftharpoons \quad NO \quad + \quad \text{other products} \qquad (3.4)$$
$$N\text{-complex} \quad + \quad NO \quad \rightleftharpoons \quad N_2 \quad + \quad \text{other products} \qquad (3.5)$$

In a reducing flame, the OH-radicals react relatively quickly with hydrogen, forming water ; the formation of NO is thus depressed.

3.2.3   *Prompt NOₓ* : This is produced by the formation first of intermediate HCN via the reaction of nitrogen radicals and hydrocarbons, followed by the oxidation of the HCN to NO. The formation of prompt NO_x has a weak temperature dependence and a short lifetime of several microseconds ; it is only significant in very fuel-rich flames. The temperature dependence of each of these three sources for a coal-fired furnace is given in Figure 3.2. The formation of NO and NO_2 in combustion processes and their subsequent reactions in the free atmosphere are summarized in Table 3.1.
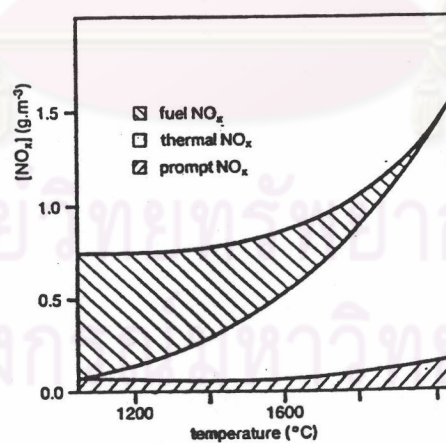
Figure 3.2 The temperature dependence of the three sources of NO

for a coal-fired furnace[1]

Table 3.1 Formation of NO and NO_x in combustion process [1]

Nitrogen Oxide	Area of formation	Mechanism/Reaction	Mainly dependent on
Thermal NO	Flame Afterburner (all kinds of fuel)	after Zeldovich [31] a) Excess Oxygen $O+N_2 = NO+N$ b) Fuel rich $N+OH = NO+H$	Concentration of O-atoms from O_2 dissociation ; residence time $(T>1300^oC)$
Prompt NO	Flame (all kinds of fuel)	$CN+H_2 = HCN^{1)}+H$ $CN+H_2O = HCN^{1)}+OH$ $CH+N_2 = HCN^{1)}+N$	Concentration of O-atoms from combustion ; O_2 concentration
Fuel NO	Flame (coal, heavy fuel oil)	via CN-compounds e.o., partly unknown.	O_2 concentration ; residence time
NO_2	Flame	after Fenimore [32] $NO+HO_2 = NO_2+OH$	Quenching of com-bustion reaction (gas turbines)
	Smoke ducts Chimneys	after Bodenstein [31] $2NO+O_2 = 2NO_2$	O_2 and NO concentration residence time $(T<650\ ^oC)$
	Free atmosphere	$NO_2+hv = NO+O$ $O+O_2+M^{2)} = O_3+M^{2)}$ $NO+O_3 = NO_2+O_2$	O_2 concentration ; light intensity ; residence time ; air pollution

1) Reaction products from which NO is formed

2) $M = N_2, O_2, H_2O$ or CO_2

3.3 Reduction of NO_x by catalyst technology

NO_x consists primarily of nitric oxide and nitrogen dioxide which are produced in all combustion process by the conversion of nitrogen and fuel-bond nitrogen. Nitrogen dioxide is linked to causing bronchitis, pneumonia, susceptibility to viral infection, and alterations to the immune system. Nitric oxide is not only produced by the burning of fossil fuels, but also by lighting, microbial decomposition of proteins in the soil, and volcanic activity. Once produced, nitric oxide is rapidly oxidized by ozone, OH, or HO_2 radicals to form the higher oxide of nitrogen, such as NO_2, HNO_3, and HO_2NO_2. Thus, if nitric oxide is prevented from entering the atmosphere, most of the downstream effects of NO_x pollution can be eliminated.

3.3.1 Selective catalytic reduction of NO_x [6]

There are a number of commercial approaches to NO_x removal (Figure 3.3) which include adsorptive, thermal and catalytic. The thorough review in 1988 by Bosch and Jassen is an excellent source for further details. Alternatively one can try to minimize NO_x formation with more efficient burner designs, nitrogen content of the fuel, or the addition of more oxygen to the fuel. Among the catalytic approaches selective catalytic reduction (SCR) is growing in application and is considered BACT (Best Available Control Technology) [4].
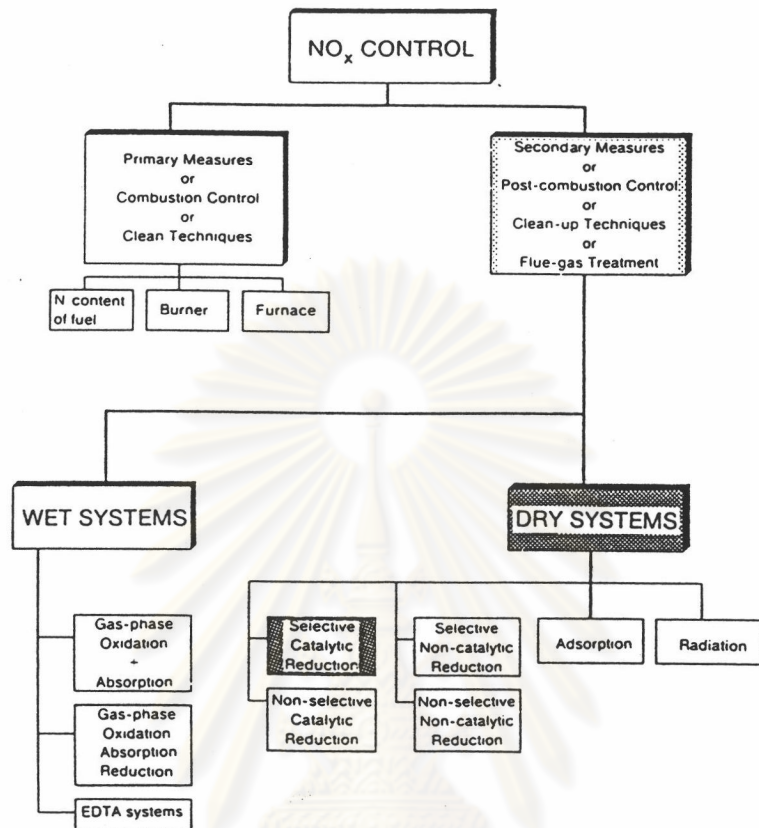
**Figure 3.3** Available techniques to decrease emission of NO_x [4]

Selective catalytic reduction (SCR) of NO_x using NH_3 was first discovered in 1957. The discussion that follows is a historical perspective of the development of SCR technology. It was discovered that NH_3 can react selectively with NO_x, producing elemental N_2 over a Pt catalyst in excess amounts of oxygen. The major desired reaction are :

$$4NH_3 \quad + \quad 4NO \quad + \quad O_2 \rightleftharpoons 4N_2 \quad + \quad 6H_2O \qquad (3.6)$$

$$4NH_3 \quad + \quad 2NO_2 \quad + \quad O_2 \rightleftharpoons 3N_2 \quad + \quad 6H_2O \qquad (3.7)$$

One undesirable reaction produces N_2O which, given its strong infrared absorptivity, is considered to be a powerful greenhouse gas :

$$2NH_3 \quad + \quad 2O_2 \rightleftharpoons N_2O \quad + \quad 3H_2O \qquad (3.8)$$
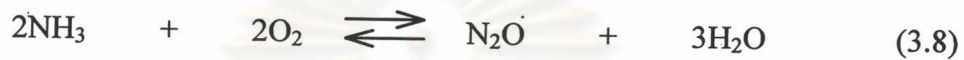
The injected ammonia can be wasted by catalytic partial oxidation to elemental nitrogen. This is a nonselective reaction :

$$4NH_3 \quad + \quad 3O_2 \rightleftharpoons N_2 \quad + \quad 6H_2O \qquad (3.9)$$
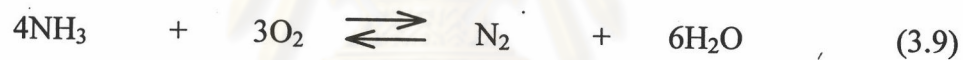
It can also be completely oxidized to NO, another nonselective reaction :

$$4NH_3 \quad + \quad 5O_2 \rightleftharpoons 4NO \quad + \quad 6H_2O \qquad (3.10)$$

At temperatures below about 100-200°C, the ammonia can also react with the NO_x present in the process gas producing explosive NH_3NO_3 :

$$2NH_3 \quad + \quad 2NO_2 \quad + \quad H_2O \rightleftharpoons NH_4NO_3 \quad + \quad NH_4NO_2 \qquad (3.11)$$

This reaction can be avoided by never allowing the temperature to fall below about 200°C. The tendency for formation of NH_4NO_3 can also be minimized by metering into the gas stream less than the precise amount of NH_3 necessary to react stoichiometrically with the NO_x (1 to 1 mole ratio). By doing so, there is little excess NH_3 that can "slip" out of the reactor.
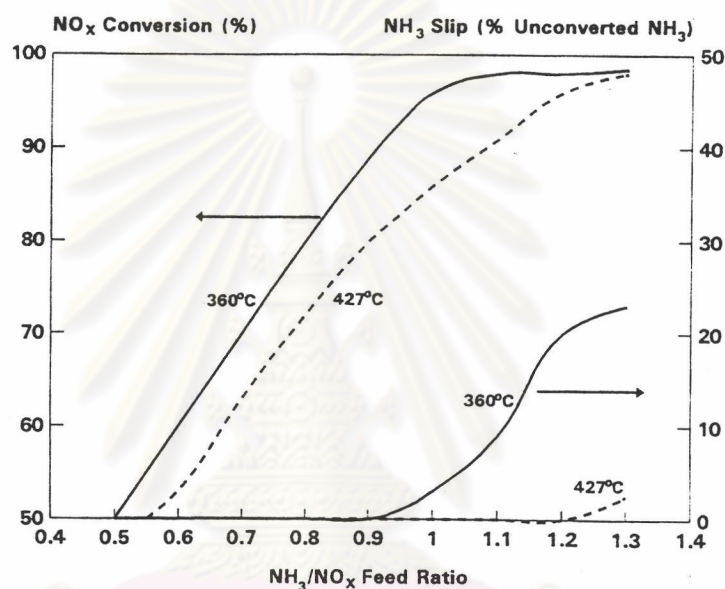

Figure 3.4 Effect of NH_3/NO_x conversion and NH_3 slip
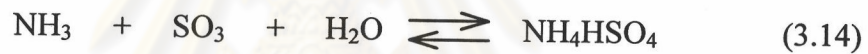
for V_2O_5/TiO_2 SCR catalyst [6]

From Figure 3.4., it is apparent that ratios much greater than 1 result in significant NH_3 slip. In all applications, there is always a specification on permitted NH_3 slip. Frequently, this is < 5-10 vppm.

When sulphur is present in the flue gas, such as in coal-fired boilers or power plants, in petroleum-derived liquid fuels such as distillate or diesel, the oxidation of SO_2 to SO_3 (equation (3.12) and (3.13)) results in formation of H_2SO_4 upon reaction

with H_2O. Obviously, this results in condensation downstream and excessive corrosion of process equipment.

$$2SO_2 \quad + \quad O_2 \quad \rightleftharpoons \quad 2SO_3 \qquad (3.12)$$

$$SO_3 \quad + \quad H_2O \rightleftharpoons H_2SO_4 \qquad (3.13)$$

The reaction of NH_3 with SO_3 also results in formation of $(NH_4)_2SO_4$ and/or NH_4HSO_4 (equation (3.14) and (3.15)), which deposits on and fouls downstream process equipment such as heat exchangers and causes a loss in thermal efficiencies.

$$NH_3 \quad + \quad SO_3 \quad + \quad H_2O \rightleftharpoons NH_4HSO_4 \qquad (3.14)$$

$$2NH_3 \quad + \quad SO_3 \quad + \quad H_2O \rightleftharpoons (NH_4)_2SO_4 \qquad (3.15)$$

Few application of SCR NO_x catalysts existed until the early 1970s, when reduction of the emission of NO_x became an important control issue for stationary power sources. The Pt technology was not applicable in this exhaust temperature region (i.e., $> 250^{\circ}C$) because of its poor selectivity for NO_x reduction at these higher temperature, so it was during this period that the base metal catalysts were invented. Figure 3.5 shows a composition of the operating temperature ranges for the various catalyst technologies available for SCR NO_x. Note that the Pt catalysts lose selectivity above 250 $^{\circ}C$. At $> 250^{\circ}C$, V_2O_5/Al_2O_3 catalyst was used first. However, its use was restricted to sulfur-free exhaust gases because the alumina reacted with SO_3 to form $Al_2(SO_4)_3$ and deactivated the catalyst. This problem led to another key development-

the use of a nonsulfating TiO_2 carrier for the V_2O_5, which then became the catalyst of choice. These catalysts functioned at higher temperatures and over a broader range than Pt (see Figure 3.5). Finally, quite recently , zeolite based catalysts have been developed that function at higher temperatures.
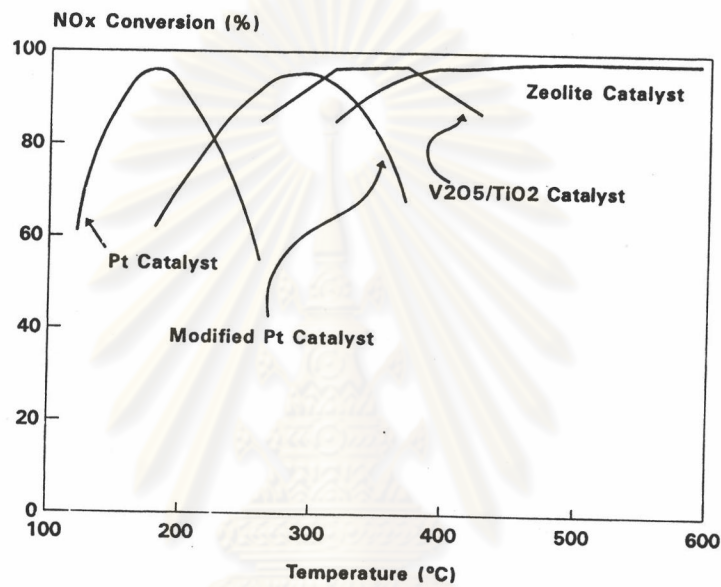

Figure 3.5 Operating temperature windows for different SCR catalyst

formulations [6]

SCR catalysts can be prepared in a number of different geometric structures. Some are extruded into pellets or homogeneous monoliths, while others are supported on parallel metal plates or ceramic honeycomb structures, and still others are fixed on a wire mesh. The appropriate structure depends on the end-use application as discussed below.

Table 3.2 SCR NO_x catalyst technologies [6]

Company	Catalyst description	Operating temperature (°C)
Babcock Hitachi	V/Ti Metal plate	240-415
Camet	Precious metal /Metal monolith	225-275
Cormetech	V/Ti/ Extruded monolith	200-450
Engelhard	Precious metal/Ceramic monolith	175-320
	V/Ti /Ceramic monolith	300-440
	Zeolite/Ceramic monolith	440-590
Hitachi Zosen	V/Ti/Extruded monolith	330-420
	V/Ti/Wire mesh	330-420
IHI	V/Ti/Extruded monoith	200-400
JMI	V/Ti/Metal monolith	340-425
KHI	V/Ti/Extruded monolith	300-400
MHI	V/Ti/Extruded monolith	200-400
Norton	Zeolite/Extruded monolith	220-520
Steuler	Zeolite/Extruded monolith	300-520
UBE	V/Ti/Extruded monolith	250-400

From the table above, the active catalytic component and temperature ranges may be classified as indicated below :

3.3.1.1. Low temperature

At low temperatures, SCR equation (3.6) and (3.7) dominate, so NO_x conversion increases with increasing temperature as shown in Figure 3.5. At about 225-250°C, the rate of equation (3.9) and the oxidation of NH_3 to NO_x and H_2O

becomes dominant that the conversion versus temperature plot reaches a maximum and being to fall. To utilize such a Pt-based, one must control the temperature of the process gas to above about 200°C to avoid NH_4NO_3 formation (equation (3.11)) but not to exceed about 225°C, where the catalyst loses its selectivity toward the NO_x reduction reaction. This narrow window for temperature control adds a great deal of expense and complexity to the overall process design. Consequently, this technology is not commonly used today.

There has emerged a low-temperature process for NO_x abatement of tail gas from nitric acid plants. This catalyst operates at inlet temperatures of 180-200 °C. The process utilizes NH_3 injection with four beds of catalyst. Two of the beds are composed of oxides of Cu and Ni on γ-Al_2O_3 cylinders. The two other beds are composed of Pt on γ-Al_2O_3. The space velocity is reported to be 15,000 hr^{-1} and with NO_x reduced by 92-95 %.

A Pt catalyst supported on a stainless steel substrate with 320 cell per square mesh is also commercially available for gas turbine applications. It simultaneously removes NO_x by reduction with injected NH_3 and also oxidizes CO and HC at a catalyst inlet temperature of less than 280°C.

3.3.1.2. Medium temperature

Medium temperature V_2O_5-containing catalysts operate best in a temperature range between 200 and 450 °C. This has the obvious advantage of a

broader operational range than Pt. However, as shown in Figure 3.5, it too shows a maximum followed by a decline in NO_x conversion where the catalyst loses selectivity. NO_x conversion initiates at about 225°C, continues to rise to a plateau at about 400°C, and then fall as the rate of ammonia oxidation and decomposition (equation (3.12) and (3.13)) being to dominate.

From the discussion above, it is clear that selectivity is lost above about 425°C. The exposure temperature of this catalyst must not exceed about 450-475°C. The active anatase phase of TiO_2 with a surface area of 80-120 m^2/g irreversibly converts to rutile with a surface area of less than 10 m^2/g.

3.3.1.3. High temperature

The suitability of zeolite catalysts for SCR above 450°C has been known since the 1970s, when the zeolite mordenite was identified as an active SCR catalyst. Mordenite has a well defined crystalline structure composed of a SiO_2-to-Al_2O_3 ratio of about 10. Commercially available zeolite SCR catalysts can operate at temperatures as high as about 600°C. When NO_x is present, this catalyst does not oxidize ammonia to NO_x according to equation (3.9). Therefore, unlike the Pt and V_2O_5 catalysts, its selectivity toward NO_x conversion continually increases with temperature as shown in Figure 5.
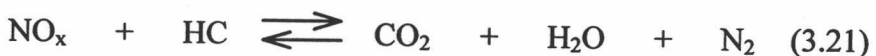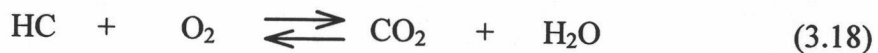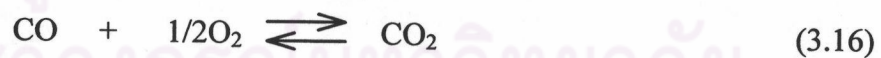
At exposure temperatures above about 600°C, in a high water content process stream, zeolites tend to deactivate by a process called de-alumination whereby

the Al^{+3} in SiO_2-Al_2O_3 framework migrates out of the structure. This leads to permanent deactivation and, in the extreme case, collapse of the crystalline structure.

3.3.2 *Nonselective catalytic reduction of NO_x* [6]

One of the earliest techniques used to abate NO_x emission from engines and nitric acid plants was to deplete the oxygen by operating the engine near stoichiometric or by adding a hydrocarbon or purge gas to deplete the oxygen via a chemical reaction in the exhaust. For stationary engine operation, the engine is normally operated near stoichiometric conditions, whereby the catalytic chemistry is very similar to automotive three-way catalyst technology. A typical response of engine emission from a natural gas fired stationary engine is give in Figure 3.6. The main differences from this application relative to automotive exhaust control are in the operating conditions (temperature, steady-state operation, and so forth) and the aging phenomenon. A typical application of engine nonselective catalytic reduction (NSCR) of NO_x would be the natural gas decompression engine used on gas pipelines or for small co-generation engines.

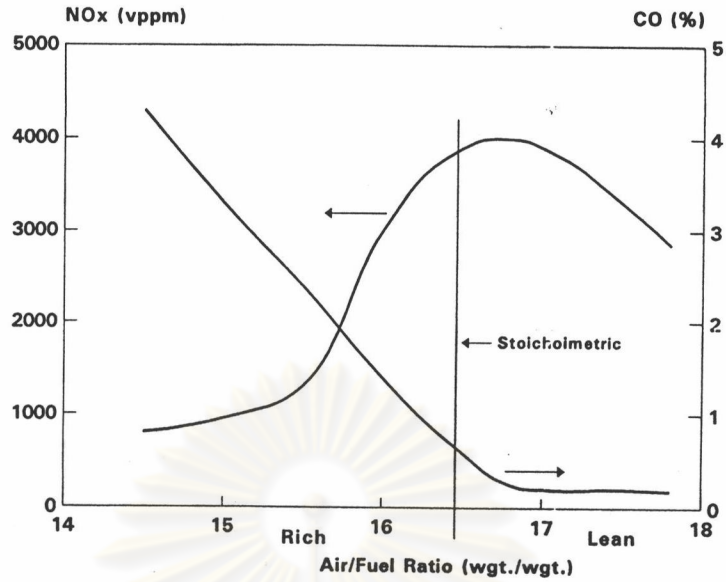The major reactions involved NSCR NO_x are as follows :

$$CO + 1/2O_2 \rightleftharpoons CO_2 \tag{3.16}$$

$$H_2 + 1/2O_2 \rightleftharpoons H_2O \tag{3.17}$$

$$HC + O_2 \rightleftharpoons CO_2 + H_2O \tag{3.18}$$

$$NO_x + CO \rightleftharpoons CO_2 + N_2 \tag{3.19}$$

$$NO_x + H_2 \rightleftharpoons H_2O + N_2 \tag{3.20}$$

$$NO_x + HC \rightleftharpoons CO_2 + H_2O + N_2 \tag{3.21}$$

Figure 3.6 Emissions of natural gas fueled stationary engine
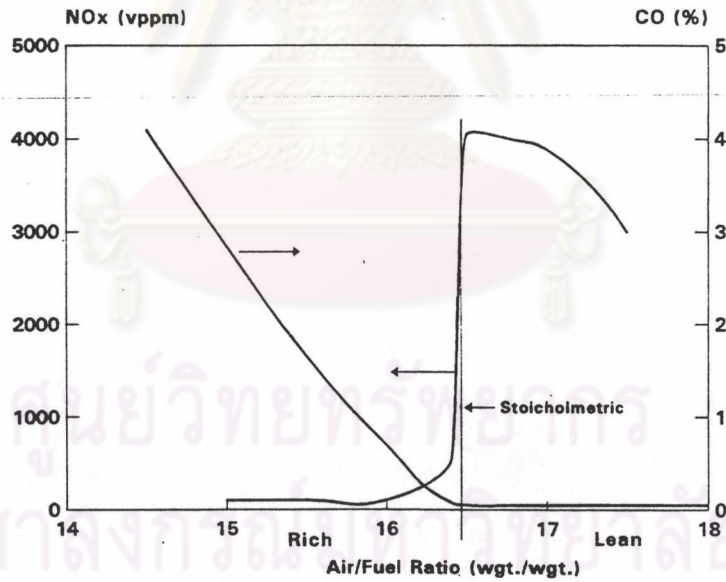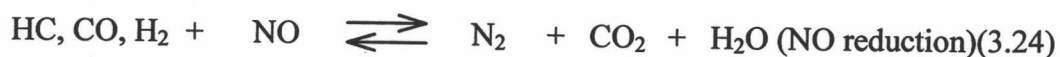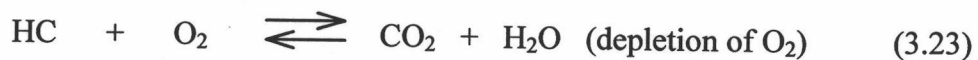
as a function of air-to-fuel ratio [6]

Figure 3.7 Emissions of natural gas fueled stationary engine

with an NSCR system [6]

$I17366537$

A typical commercial catalyst ranges from 0.1 to 0.5 percent platinum, plus rhodium supported on a high surface area γ-Al_2O_3 washcoated onto a 200 to 400 cpsi ceramic honeycomb. Usually, the reactor operates at 50,000 hr^{-1} to 100,000 hr^{-1} space velocity. The operating temperatures range from 450 to 900°C, with the co-generation applications having the higher range.

The other major application of NSCR technology is in the abatement of the exhaust gas from nitric acid plants. This so-called tail gas abatement is one of the earliest techniques to abate NO_x emission from oxidizing environmental. Nitric oxide emissions produced during the manufacture of nitric acid by high-temperature catalytic oxidation of NH_3 can be conveniently abated by a nonselective process. Reddish-brown NO_2 is emitted into the atmosphere in the presence of excess air. Since the environment is oxidizing, and NO_2 must be reduced to N_2, it is necessary in NSCR to first consume all the excess O_2 by combustion by adding a fuel such as CH_4 (natural gas), LPG, or purge gas. The NO_2 is then catalytically reduce to N_2 by residual fuel or its by-products (i.e.,CH_4, CO and so on). Tail gas abatement is accomplished through a three-step process as shown by the following reactions :

$$HC + NO_2 \rightleftarrows NO + CO_2 + H_2O \qquad (3.22)$$

$$HC + O_2 \rightleftarrows CO_2 + H_2O \text{ (depletion of } O_2) \qquad (3.23)$$

$$HC, CO, H_2 + NO \rightleftarrows N_2 + CO_2 + H_2O \text{ (NO reduction)} (3.24)$$

As evident from the reddish-brown plume, the tail gas contains predominantly NO_2. The catalyst ranges from 0.3 to 0.5 percent platinum, plus small amounts of

rhodium deposited on an alumina carrier upon a ceramic honeycomb structure. The operating temperature varies, depending on the fuel used to deplete the oxygen. Purge gas, which contains some H_2 and CO, operates at 300-350°C, while natural gas requires a high temperature of 500-550°C. LPG usually required 350-450°C. Normally, these reactors operate at 50,000 to 100,000 hr^{-1} space velocity. A hybrid low NO_x process is commercially available. It is composed of a thermal O_2 burn-out step, followed by NO_x reduction using added by hydrocarbon fuel, and a final oxidation step to remove excess hydrocarbon and CO.

3.4 Titanium oxide supported vanadium oxide

3.4.1 Vanadium oxide

Supported vanadium oxide catalysts are important in industrial process. The reactivity of supported vanadium oxide catalysts has been examined for several catalytic reactions (e.g., the oxidation of o-xylene, 1,3-butadiene, methanol, carbon monoxide, ammoxidation of aromatic hydrocarbons(toluene and 3-picoline), selective catalytic reduction (SCR) of nitric oxide, and partial oxidation of methane). In many cases they are doped with promoters to improve their activity and/or selectivity, and supports are used to improve mechanical strength, thermal stability and lifetime. Supports were long believed to be inert in catalytic reactions ; it is know now, however, that the structure and the composition of the materials used as supports can influence the activity and selectivity of the active phase to a marked degree.

A number of researchers in 1970s believed that the two-dimensional metal oxide overlayers that formed on oxide supports were unstable and that the metal oxide overlayers needed an extended three-dimensional (bulk) structure to be effective catalysts. The concept of metal oxide monolayers lay in the realization that unique surface metal oxide species were present and stable on the surface of oxide supports. In supported vanadium oxide catalysts, the vanadium oxide phase on the surface of an oxide support (e.g. TiO_2) is the active phase and is usually more active than bulk crystalline vanadium pentoxide (V_2O_5).

3.4.1.1 Vanadium oxide structural chemistry [5]

Vanadium has the electron configuration $3d^3 \, 4s^2$ in addition to the completed inner electron shells. Vanadium (V), oxide compounds exist in a number of different coordinations and structures. The radius ratio of the vanadium (V) atom to the oxygen atom is rather large to form four coordinated structures and rather small for forming six coordinated structures. Perhaps for this reason vanadium (V) oxide compounds are present in nature as four, five, or six coordinated species. To appreciable the different structural properties of vanadium (V) oxide, it is beneficial briefly to touch upon its aqueous and solid state chemistry.

I <u>Vanadium (V) oxide structures in aqueous media</u>.

The different possible coordinations of vanadium (V) oxide are demonstrated in the aqueous chemistry of the vanadium (V) ion in solution of different pH and ionic strength. The vanadium (V) ion is the stable oxidation state in

aqueous solutions in the presence of air. Twelve different vanadium (V) oxide species are know to exist in aqueous solutions. At high pH values (basic region) and low vanadium (V) ion concentrations, the vanadium (V) oxide species is four coordinated and isolated (VO_4^{3-}) ; at low pH values and high vanadium (V) ion concentrations, the vanadium (V) oxide species is present as polymerized and six coordinated decavanadates, $V_{10}O_{28-z}(OH)_z^{z-6}$. Intermediate values of pH and vanadium (V) ionic concentrations give rise to various levels of polymerization and protonation of four and six coordinated vanadium (V) oxide species (e.g., $V_2O_6(OH)^{3-}$, $V_3O_9^{3-}$, $V_{10}O_{27}$ $(OH)^{5-}$).

II Vanadium (V) oxide structures in the solid state.

Vanadium (V) oxide structures in solid are usually very distorted in comparison with the aqueous phase structures. However, certain examples exist in the solid state that bring out some of the regular coordinations of the vanadium (V) oxide structures. Vanadium (V) oxide structures can be generally categorized as four coordinated vanadates (orthovanadates, pyrovanadates, and metavanadates), five coordinated vanadates, and six coordinated vanadates.

Orthovanadates containing isolated VO_4 units include $Pb_5(VO_4)Cl$, $BiVO_4$, Na_3VO_4, and α-$Zn_3(VO_4)_2$ and are the least distorted of the four coordinated vanadates. These orthovanadates are characterized by possessing nearly equal vanadium oxygen bond length ranging from 1.69 to 1.77 $^\circ$A. Pyrovanadates contain V_2O_7 dimeric units and are found in $Cd_2V_2O_7$, α-$Zn_2V_2O_7$, and α-$Mg_2V_2O_7$. The

presence of a V-O-V bridge results in a short vanadium oxygen terminal bond length, 1.658 to 1.672 $^{\circ}$A. The α-$Mg_2V_2O_7$ structure is not an ideal pyrovanadate, but possesses a long fifth V-O bond (2.4-2.9 $^{\circ}$A). Metavanadates posses polymeric chains of -(VO_2)-O- units and can be found in NH_4VO_3 and α-$NaVO_3$. The two terminal vanadium oxygen bonds in the VO_2 units range from 1.63 to 1.67 $^{\circ}$A, and the vanadium oxygen distances in the V-O-V bridging bonds are 1.8 $^{\circ}$A.

Six coordinated vanadium oxide structures are found in PbV_2O_6, V_2O_5, and $Na_6V_{10}O_{28} \cdot 18H_2O$. two distinct types of VO_6 units can be found in PbV_2O_6. The structure of V_2O_5 contains chains of highly distorted VO_6 units with one short apical V-O bond at 1.58 $^{\circ}$A, an opposing long V-O bond at 2.78 $^{\circ}$A, and four bridging V-O bonds lying roughly in a plane at 1.78, 1.88 (x2), and 2.02 $^{\circ}$A. The decavanadate unit in $Na_6V_{10}O_{28} \cdot 18H_2O$ contains essentially five different VO_6 units. Four of these VO_6 units posses terminal vanadium oxygen bonds similar to V_2O_5 and each of the four terminal V=O bonds are distinct from each other. The fifth VO_6 unit does not, however, posses a terminal vanadium oxygen bond, and all of its oxygen atoms are part of V-O-V bridging bonds.

In the solid state, vanadium and oxygen form different types of vanadium oxides in addition to V_2O_5. In these vanadium oxides, vanadium possesses oxidation states lower than 5.

3.4.2 *Titanium oxide* [5]

Titanium oxide (TiO_2) or titania occurs naturally in three crystalline forms : anatase, rutile, and brookite. The last is not common. Catalytically, the anatase form is the most important in that it has the highest surface area (50-80 m^2/g), and is thermally stable up to about 500 ^{o}C. The rutile structure has a low surface area (<10 m^2/g), and can form from anatase at about 550 ^{o}C, resulting in occlusion of the vanadia and, ultimately, deactivation. Thus, anatase is the preferred form for use as a catalyst support in a vanadia-titania catalyst such as conversion of o-xylene to phthalic anhydride, possibly in part because of better wetting characteristics for the vanadia. However, anatase typically has a higher surface area than rutile, which may account at least in part for its preference here and in other application.

V_2O_5/TiO_2 is one of the best catalysts for reduction of nitric oxide with ammonia, an important process for minimizing NO_x emission from exhaust gases from power plant. Titania is more acidic than alumina and, unlike alumina, is not readily sulfated in the presence of sulfur oxides (SO_x). This may be of some advantage in the Claus process for conversion of H_2S to elemental sulfur by partial oxidation.

3.4.3 Molecular structures of titanium oxide supported vanadium oxide
catalysts

Knowledge of the structure of the surface vanadium oxide species in supported vanadium oxide catalysts is critical to the fundamental understanding of the surface vanadium oxide phase-support and surface vanadium oxide phase-reactant gas interaction. The structure of the surface vanadium oxide phase in supported vanadium oxide catalysts depends on both the particular gas and solid environment. There is now no doubt that VO_x monolayer species, as well as many other related species, can be stabilized on the surface of oxides, particularly TiO_2 in the anatase form. The interaction which results in the stabilization can be viewed either in terms of minimization of surface free energy or in terms of the formation of new chemical compounds. The actual structure present will depend amongst other things on the chemical nature and crystal structure of support, the vanadium loading, and on the presence of adventitious impurities. What remains unclear is the extent to which TiO_2 as support produces a favorable modification to the energy of the V=O bond, in a way which other oxides cannot, and to what extent its superiority lies simply in its ability to create stable monolayers. VO_x when present at very low concentration (<1 wt. % V_2O_5) on TiO_2 (anatase) forms isolated species ; at high concentrations, but still below the theoretical monolayer capacity, a two-dimensional surface phase is thought to develop ; and a disordered V_2O_5 phase exists at concentrations above the monolayer point. Finally, a paracrystalline V_2O_5 has been recognized at very high loadings.

It is generally believed that the vanadia layer structure exposes the (010) plane and the V=O groups preferentially because of the excellent match of the vanadate unit and the anatase structure. It has been proposed that on the (001) plane of anatase, vanadium exists as monovanadate $(VO_4)^{n-}$ groups bonded to the surface as [33] (see Figure 3.8):
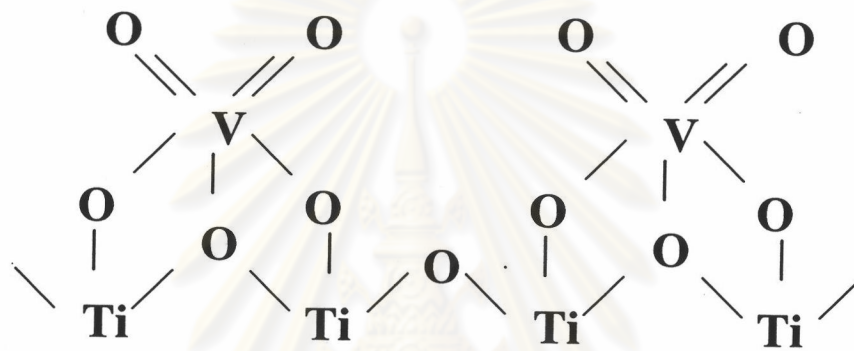

Figure 3.8 The structure of titanium oxide supported vanadium oxide [33]

In this form, the V ion occupies roughly a position which another Ti ion would occupy if the bulk structure continues. The V-O bridging bond length of 0.190 nm. is very close to the Ti-O bond length of 0.193 nm. Indeed, EXAFS/XANES studies show that on anatase, the basic structure unit of vanadium contains two terminal V=O bonds of a bond length of 0.165 nm, and two bridging V-O bonds of 0.190 nm. The picture is also consistent with the observation that an average of one oxygen ion per vanadium can be readily removed on reduction.
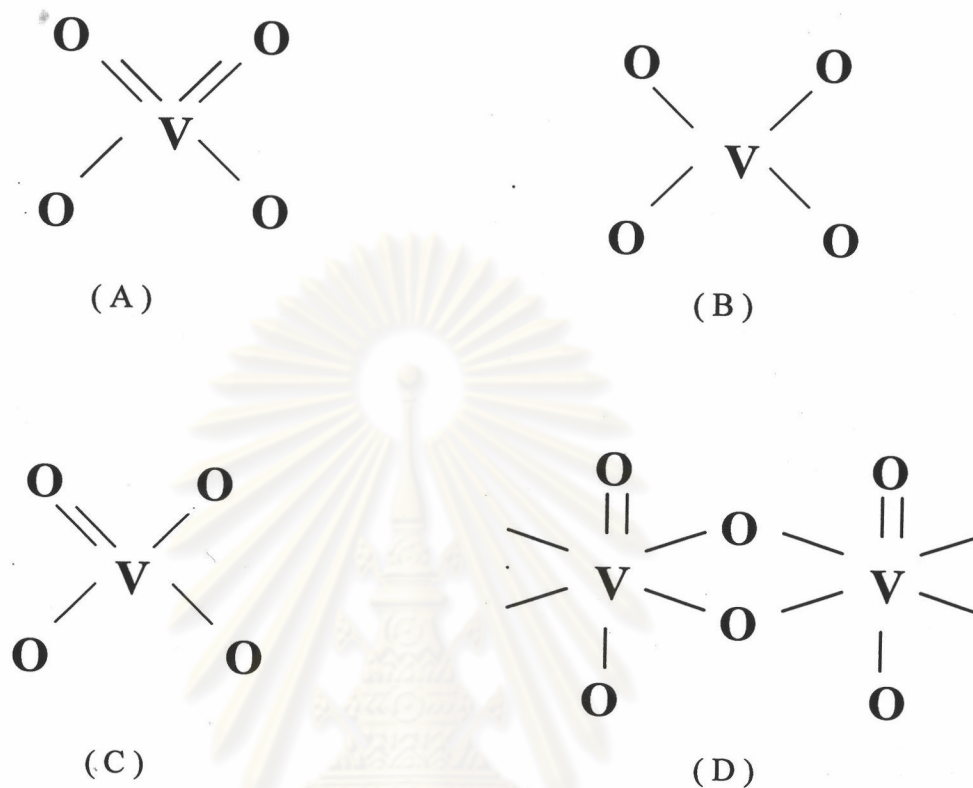
Figure 3.9 Possible structure of VO_x species [3]

From laser Raman and FT-IR spectroscopy also serve to distinguish clearly between monolayer species and other forms. The characteristic sharp Raman peak at 995 cm^{-1} due to the V-O-V vibration only appears when more than a monolayer is present and also indicates the end of the monolayer phase. Bands observed within the monolayer region suggest the presence of tetrahedral vanadate or vanadyl species on TiO_2 ; these are isolated at low loading, have been formulated as structure (A) in Figure 3.9. However, the monolayer species are capable of reacting further with a source of vanadyl groups and also show marked acidic properties, strongly suggesting that OH groups are present. Under hydrous conditions the VO_x species may be

properly formulated as structure (B) or (C) in Figure 3.9, and the evidence for acidic-OH groups sited above may relate to the hydrate forms. On heating in a dry atmosphere there may be dehydration to structure A, to an octahedral polyvanadate species such as structure D or to a simple vanadyl species. The ratio of V : Ti in the monolayer is approximately unity [3].